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COMPOSITES IN SIMULATED MARINE ENVIRONMENTS

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EXECUTIVE SUMMARY

The Naval Facilities Engineering Service Center (NFESC), under the sponsorship of the Office of Naval Research (ONR), studied the effects of laboratory simulated marine climates on the mechanical properties of several commercial composites. These composites included glass-reinforced polyesters, vinylesters, phenolics and an epoxy (epoxy-polyamide). The composites were based on thermoset resins and all samples were pultruded by one manufacturer in order to standardize the tests.

The sample specimens, prepared from glass fiber and the different resins, were cut into 10-inch (0.5 inch wide) strips. The strips were placed in different chambers for simulated weathering, including:
(1) Oxygen (100%) and salt water spray (100ºF) for 12 months
(2) Oxygen (100%) and salt water submersion (100ºF) for 12 months
(3) Cold freezer (-4ºF) for 9 months
(4) Salt fog tank (95ºF) for 28 days, 12 months and 18 months
(5) Dry heat oven (95ºF) for 120 days
(6) Ultraviolet exposure unit (70ºC or 158ºF cycles) for 90 days

The test specimens were exposed from 28 days up to 18 months, and were then tested for variations in mechanical properties. Specimens were tested using ASTM test methods for thermomechanical properties:
(1) flexural strength (ASTM D 790)
(2) tensile strength (ASTM D 3039)
(3) flexural storage modulus and glass transition temperature by DMA (dynamic mechanical analysis) (ASTM D 5023)

Results indicate that exposure to seawater causes the greatest deterioration of the flexural and tensile strengths of the composites. Submersion in an oxygen-rich seawater environment may slightly accelerate the deterioration. Average flexural strength losses were 27% after 12-month salt fog exposure and 34% in the 12-month accelerated oxygen-rich environment. Since the salt fog exposure is a simpler test set-up, it is recommended for future evaluations.
Tensile tests after salt fog exposures at 28 days and 18 months showed degradations around 10% for vinylesters and polyesters, around 26% for phenolic II, and up to 39% for the epoxy. The oxygen-rich environment did seem to somewhat accelerate the degradation, mostly for the epoxy (54% loss versus 39%). Little change was observed in the glass transition temperature, T_g.
Exposure to moderate dry heat, ultraviolet radiation, and cold storage in the freezer had little or no effect. Heat and UV radiation actually appeared to further cure some of the composites. Storage in the freezer apparently arrested the curing process but did not embrittle the polymers.

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1. INTRODUCTION

The objective of this study was to determine variations in mechanical properties of several types of commercial polymer composites for infrastructure applications, before and after exposure to simulated weathering conditions in the laboratory. This work was funded by the Office Naval Research (ONR) as a 6.2 applied research project, in support of the Naval Facilities Engineering Command (NAVFACENGCOM).

Composites are especially attractive to the Naval Shore Establishment to replace traditional structural materials, such as steel, that corrode in harsh marine environments. Examples include pier piling, handrails, utility pipes and pipe hangers, ladders, cat-walks under piers, reinforcing bars for concrete, and fender systems. Limited durability studies were already conducted by NFESC, in the laboratory and at the Advanced Waterfront Technology Test Site (AWTTS) [1-3]. Although qualitative differences in weathering properties were observed for vinylesters and polyesters, it was determined that additional quantitative data was needed, using composite coupons and standardized tests. A series of uniform samples, weathering (exposure) conditions, and physical test methods were designed, to allow direct comparison of major classes of composites for waterfront applications. It is hoped that the present results will be helpful to field personnel in selecting durable materials for Naval shore construction.

2. DURABILITY ISSUES: STATE-OF-THE-ART

Although fiber reinforced polymer (FRP) materials do not decay in the same fashion as the steel reinforcements they replace, they still present durability issues. In the U.S., the California Department of Transportation (CALTRANS) and the International Conference of Building Officials (ICBO) were the first to require durability testing of FRP materials used in seismic upgrades.   CALTRANS durability tests include the following environmental exposures: humidity, salt water, diesel fuel, ultraviolet, alkali solution, elevated temperature (140ºF), and freeze-thaw cycling [4-7]. ICBO also requires environmental durability testing with exposures to water, salt water, alkali, dry heat, and freeze-thaw (other requirements, like fire, are beyond the scope of this report) [8].

Several countries now have codes that provide design guidelines with FRP materials, and address durability issues, in particular Japan [9, 10], Canada [11, 12, 13], and the United States [14, 15]. In the U.S. these guidelines are being completed by the American Concrete Institute Committee on Fiber Reinforced Polymers (ACI 440). NFESC (Malvar) is an active member of ACI 440, and part of the Federal Working Group on Composite Materials sponsored by the National Institute of Standards and Technology (NIST), the Tri-Service Composite Group, and the Durable Advanced Materials Systems User Group sponsored by the U.S. Army Engineer Research and Development Center Construction Engineering Research Laboratory (ERDC-CERL). These groups have focused their recent research on the durability of FRP. In 1998, the National Science Foundation also launched a request for proposals in the area of materials durability, and in particular composites (NSF 98-42, Long Term Durability of Materials and Structures: Modeling and Accelerated Techniques Initiative,

Announcement for FY 1998, available at http://www.nsf.gov/pubs/1998/nsf9842/nsf9842.txt).
NFESC served as a reviewer for this initiative.

3. DURABILITY ISSUES IN THE WATERFRONT

Several industries have replaced steel or aluminum structures with polymer composites, because of their strength and resistance to corrosion [16]. In infrastructure applications, reinforcing bars and prestressing tendons, as well as structural shapes, and gratings are being replaced, and FRP wraps are being used for rehabilitation and upgrade of existing structures [1, 2]. While carbon reinforced FRP (CFRP) composites are relatively very durable, glass FRP (GFRP) composites are not [17]. However, since GFRP materials are much cheaper, they are often used, raising the need for further understanding of their durability characteristics. For Navy applications, waterfront exposure is of most concern.

GFRP composites may last many years before showing signs of wear or degradation. However, they can deteriorate when exposed to sunlight, smog, acid rain, hot and cold temperatures, and long term exposure to, or immersion in, ocean water. Seawater exposures, either salt fog or oxygen-rich salt water, have been shown to result in the most severe degradation of material properties. This has been confirmed by several authors. For example Karbhari and Engineer [18] exposed samples to fresh water, seawater, cold, and freeze-thaw, and found the seawater exposure to be most detrimental. Chin et al. [19] also exposed polymer materials to ultraviolet radiation, moisture, heat, and high pH. The most severe degradation was observed to take place for alkaline and saline environments. The effect of UV on strength loss was reported as insignificant. As reported by Liao et al. [20], the higher the temperature and the longer the exposure time to fluids, the larger the decrease in strength and modulus of FRP.

The preceding results explain the emphasis of recent durability studies on marine exposure. Not only are polymer properties affected, but the bond of the FRP to the substrate is also of concern. Sen et al. [21] studied the durability of the bond of CFRP to concrete by exposing specimens to wet/dry and thermal cycles. Under a long term exposure test it was found that the greatest material degradation occurred under hot-wet exposure conditions. Cyclic high temperature and high humidity tests are also recommended by the Architectural Institute of Japan [22]. Liao et al. [23] report that tensile strength, compressive strength and modulus of GFRP can all be degraded upon exposure to various moist and aqueous environments. Dejke [24] reports that glass fibers are known to degrade in the presence of water, and that moisture can decrease the glass transition temperature of the resin and act as a plasticizer, potentially having a significant effect on flexural strength.

The test data or specifications supplied by vendors can be of limited use because tests are done on new materials, not weathered materials. There are many types of reinforced polymers available. Table 1 gives some examples of thermoplastic composites and thermoset composites. The thermoplastics can be heated to soften and re-shape. The thermoset plastics

set irreversibly upon heating and cannot be reshaped by subsequent heating (although thermosets become flexible through their glass transition temperatures).

Depending on the chemistry of the formulation, composites may be soft or hard, brittle or flexible, electrically conducting or insulating, and susceptible or resistant to heat, oxidation, cold (freezing), or sunlight (ultraviolet or UV radiation). The properties of the final composite will depend on the following:
- Class of polymer resin and type of reinforcing agents
- Chemical additives and modifiers
- Method of manufacturing
- Percentage and orientation of the fiber reinforcement.

For example, there are several types of polyesters. Polyesters are made from phenols (or di-phenols) condensed with acid anhydrides. Acid anhydrides are di-functional carboxylic acids that have been heated to remove water. These chemicals react exothermically with alcohols and phenols to yield esters (or in the case of polymerization, polyesters).

$$\text{Phenol} + \text{acid anhydride} \rightarrow \text{polyester}$$

There are many types of phenols and bis-phenols and many types of acid anhydrides that can be reacted to make different polyesters. Polyester properties can also be modified by incorporating other chemicals into the mix (liquid phase) such as: (1) opacifiers (such as silica, alumina or titanium dioxide), (2) plasticizers (such as N-butyl phthalate), (4) fire retardants (such as phosphorus, bromine or boron derived chemicals), (5) anti-oxidants, and (6) UV stabilizers.

Polymer composite properties will also vary depending on the manufacturing methods. Composites can be made by: (1) extrusion, (2) pultrusion, (3) pressing, (4) hot stamping, (5) molding, and (6) vacuum forming. For the current study, samples were made by pultrusion, as illustrated in Figure 1.

4. TEST MATERIALS

The following glass reinforced polymer composites were chosen for the studies:
- two vinyl esters (I and II)
- two polyesters (I and II)
- two phenolics (I and II)
- one epoxy (epoxy-polyamide).

The original dimensions of each composite piece were 10" x 0.5" x 0.125" (although most actually measured 0.13 in thickness), except for the Phenolic I, which was thinner (0.093 inch).

The polymer chemical formulations were:

- **Vinyl esters I and II** – two commercial formulations containing epoxy vinyl ester resins made with bisphenol-A and styrene.

- **Isopolyesters I and II** – two commercial resin formulations made with isophthalic acid, maleic anhydride, and common glycols.

- **Phenolic I and II** – thin (0.093 inch for Phenolic I) and thick (0.13 inch for Phenolic II) samples of one commercial resin made with phenol and formaldehyde (product is a waterborne, styrene-free, phenolic resole).

- **Epoxy-Polyamide** – a commercial resin made with bisphenol-A epoxy and aromatic amine curing agents.

These seven types of glass reinforced thermoset plastic composites are readily available for use in waterfront applications. Pultruded thermoset composites were chosen because they are among the strongest, most weather resistant composites used in outdoor construction.

The composite strips were all made for NFESC by Strongwell Corporation (formerly MMFG), in Bristol, VA. The company purchased the resins and fiberglass matting from major chemical companies and prepared 6-inch wide pultruded strips. The strips had 7 plies of 3 ounce and 2 plies of 0.5 ounce continuous strand E-glass mat, with 8 plies of 113 yield E-glass rovings for the laminate design of the epoxy, polyester, and vinylester specimens. The glass content of the epoxy, polyester, and vinylester composites was 42.5% by weight. However, the rovings made up 28% of the total glass weight.

Rovings were unidirectional and run in the long (10 inch) direction. Continuous strand mat was in random orientation. The stitched mat was a combination of 0° and 90° rovings. The phenolic laminates were different due to the chemical method of preparing phenolics (condensation). Phenolic composite coupons had a 60% glass content by weight.

The sheeting was cut into smaller strips in the longitudinal direction and the edges were sealed with a varnish at the Strongwell facility. The composite samples were weighed and stamped for identification at NFESC.

5. SAMPLE PREPARATION AND EXPOSURES

The project management plan is presented below:
- Select 7 types of pultruded thermoset resins with glass fiber reinforcement.
- Cut composite into 10 x 0.5 x 0.125 inches strips and seal the edges (completed at the manufacturer's facility).
- Stamp the composite strips with letters and numbers, to identify them.
- Select 15 composite strips of each type, for each type of environmental exposure.
- Expose specimens for designated durations.

- Remove composite specimens and test for flexural (Figure 2) and tensile strength, and perform dynamic mechanical analysis (DMA). Test in triplicate and determine average, mean, and standard deviation values.
- Collect, reduce and analyze the data, and convert into graphs and bar charts for comparison of the effects on each type of composite.

The GFRP composite strips were exposed to the following:

(1) Oxygen (100%) and salt water spray (100ºF) for 12 months – Figure 3
(2) Oxygen (100%) and salt water submersion (100ºF) for 12 months – Figure 3
(3) Cold freezer (-4ºF) for 9 months
(4) Salt fog tank (95ºF) for 28 days, 12 months and 18 months – Figure 4
(5) Dry heat oven (95ºF) for 120 days – Figure 5
(6) Ultraviolet exposure unit (70ºC or 158ºF cycles) for 90 days – Figure 6

These conditions were used to simulate outdoor exposures to heat, air oxidation, ocean spray, intense sunlight, and cold weather. The high oxygen-saltwater test was a modification of a system reported for the photo-oxidation of plastics [25]. An oxygen atmosphere (100%) was used to replace air (20% oxygen) in order to accelerate the aging of the composites. Accelerated exposure tests can usually reach the same degradation as natural exposure tests, but K times faster (where K is the acceleration factor) assuming a linear rate model as indicated in ASTM E 632 (Standard Practice for Developing Accelerated Tests to Aid Prediction of the Service Life of Building Components and Materials). The salt fog chamber is a severe, but natural (tropical) exposure. Hence the oxygen-rich exposure results will be compared to the salt fog results to determine what acceleration factor, if any, was achieved. Another acceleration factor that may be considered in follow-up tests would be higher temperature.

Flexural and tensile tests were performed following the American Society of Testing and Materials (ASTM) methods D 790 (Standard Test Method for Flexural Properties of Reinforced and Unreinforced Plastics and Insulating Materials), and D 3039 (Standard Test Method for Tensile Properties of Polymer Matrix Composite Materials).   The testing equipment for flexural strength is shown in Figure 2.
The GFRP composites were also tested using dynamic mechanical analysis (DMA). DMA is an analytical technique that complements the tensile and flexural testing. DMA is used for determining thermomechanical behavior of polymeric materials, e.g., T_g (glass transition temperature) and other transitions in the polymer matrix. Viscoelastic properties of materials, i.e. the modulus (or stiffness) and damping (energy dissipation) properties are measured as those materials are deformed under periodic stress through a specified temperature range. Such measurements provide quantitative and qualitative information on the performance of materials.

5.1.   Oxygen Atmosphere (100%) and Salt Water Exposure Tests

The reaction rate (between oxygen and hydrocarbon based plastics) can increase as a function of the amount of oxygen available (e.g. 100% instead of 20% in air), and also the reaction rates can double for each 20ºF increment above room temperature (70ºF). In the present test, the temperature was kept around 100ºF, simulating natural tropical exposure, but also accelerated testing if compared to more typical ambient temperatures (70ºF). When glass reinforced polymers are exposed to air (20% oxygen), they gradually deteriorate over many years, due to chemical reactions between the polymer and the oxygen. In general terms, the carbon-hydrogen bonds (C-H) are replaced by carbon-hydroxy bonds (C-OH), which soften the resin and causes polymer chain breakage. This reaction is accelerated somewhat if the composites are placed in warm water (swelling) or exposed to sunlight (photochemical degradation).

Since there was no commercial equipment available for performing the high oxygen-salt-water exposure tests, the equipment was built (Figure 4). A large glass tank (80 gallons) and lid were constructed. Holes were cut in the lid for rubber stoppers in order to support a thermometer well, a gas diffusion tube, a gas release valve (with stopcock), and a remote oxygen sensor. The glass diffusion tube extended from the lid to the bottom of the glass tank. It was attached to a five-tube gas bubbler with fritted glass disks in order to bubble in the oxygen. Oxygen was supplied from a compressed cylinder. The bottom third of the tank was wrapped with an insulated electrical heating tape, which was connected to a variable transformer (Variac) to control the water temperature. The exterior of the glass tank was insulated with a glass wool blanket and aluminum foil to reduce heat loss.

Artificial seawater was prepared from sea-salts and de-ionized water, and was added to the tank to fill it a little less than one third. A polycarbonate rack was designed and built to hold the composite strips vertically, both in (submerged) and out (atmospheric exposure) of the salt water. The bubbling of oxygen gas through the sparger created a salt spray as well as the oxygen atmosphere.

Initially, oxygen (at about 5 psi) was run through the glass tube into the salt water for about 2 hours. This purged the tank of air. The oxygen concentration was monitored with an electronic, remote controlled sensor.   The atmosphere was maintained at 95% to 100% oxygen (0 to 5% nitrogen) by periodic addition of oxygen. All gases were vented to the hood and no ignitable materials were present during the studies.

5.2.   Cold Temperature Exposure Tests

Groups of 15 composite strips, from each of the 7 composite types, were placed on racks in the freezer section of a laboratory refrigerator. They were exposed to a temperature of –4ºF for a maximum period of 270 days (9 months). Samples kept in the freezer were expected to be weakened because of damage caused by internal stresses in the material due to the different thermal expansion coefficients of the fibers and matrix. Some recent research, however, indicates that cold alone may not result in degradation [26].

5.3. Salt Fog Tank Exposure Tests

The test chamber temperature was set to 95ºF (35ºC) and salt fog was introduced. A 5% wt. salt solution was continuously atomized into the chamber. The salt fog condensation rate was 0.65 ml/80 cm^2/hour. The measured pH of the condensate solution was 6.0. The pH was measured at room temperature after collection of the condensate and followed procedures stated in ASTM B 117 (Standard Practice for Operating Salt Spray Apparatus). Groups of 15 composite strips, from each of the 7 composite types, were placed in the chamber for 28 days, 12 months, and 18 months.

5.4. Dry Heat Exposure Tests

Groups of 15 composite strips, from each of the 7 composite types, were placed on steel racks in a Blue M oven (see Figure 5) pre-set to a temperature of 100ºF. The strips were kept in the oven for 120 days.

5.5. Ultraviolet Radiation Exposure Tests

Groups of 5 composite strips, from each of the 7 composite types, were placed on racks of a Q-UV Accelerated Weathering Unit (see Figure 6) from Q-Panel Corporation (Cleveland, OH). Samples were irradiated with UVA-340 fluorescent tubes. The exposure used was Cycle B from ASTM D 4329 (Standard Practice for Operating Light and Water Apparatus – Fluorescent UV and Condensation Type – for Exposure of Plastics). This cycle represents the most severe exposure, typically used for automotive exterior applications. It consists of 8 hours of UV exposure at 70ºC (158ºF), followed by a 4-hour condensation at 50ºC (122ºF). The other two exposure cycles in ASTM D 4329 are for general and plastic building products applications, and use a lower temperature during the UV exposure. Since all the composite strips were pigmented, half of each specimen was masked with aluminum foil so that the colors of the exposed and un-exposed halves could be compared.

6. MECHANICAL TESTING

6.1. Flexural Tests

Each of the control (unexposed) polymer composite strip types was tested in triplicate for flexural strength using the method described in ASTM D-790 (Standard Test Methods for Flexural Properties of Un-Reinforced and Reinforced Plastics and Electrical Insulating

Materials). The test specimens were supported at two points (support span) and loaded in a conventional "three point loading" configuration (ASTM D-790). The bending load (P) was recorded in pounds and the displacement (d) was recorded in inches.

The jagged region on the peaks of the actual composite curves are due to the breakage of glass fibers in the composite strip. If the curve from the weathered sample moves to the right of the original curve, the sample has become more flexible.

In a flexural test, the top (glass) fibers are in compression and the bottom fibers are in tension. Premature failure on the tension side is a reflection of glass fiber or fiber/matrix interphase degradation. Premature failure on the compression side is one indication of resin degradation, since the resin holds the fibers together and prevents buckling when under stress. Degradation of the resins in composites can also be determined from the changes in glass transition temperature (T_g) of the polymer ("glass" refers to the solid polymer, not the silica glass). The transition point (at T_g) represents the change from a brittle state to an elastic state or vice versa for amorphous materials. More information on this polymer property is discussed in the section on DMA (dynamic mechanical analysis) below.

After the controls were tested, each class of composite was exposed to dry heat, salt fog, high oxygen, cold temperature and ultraviolet radiation. After exposure, the weathered specimens were tested for flexural strengths. Flexural tests were run in triplicate for each composite type, and each weathering condition. The results were averaged and converted into plots of stress vs. displacement (Appendices A and B).

6.2. Tensile Tests

The composite strips were tested for tensile strength, before (control) and after exposure (Appendix C) following ASTM D 3039 (Standard Test Method for Tensile Properties of Polymer Matrix Composite Materials). Tests were performed on the composite strip controls, and on the composite strips exposed to the high oxygen/sea water and to the salt fog. The composite strips were exposed to the oxygen/seawater environment for 350 days. The composites were exposed in the salt fog tank for 28 days and 540 days (18 months).

6.3. Thermomechanical Tests (DMA)

For each composite type, the control specimens and the specimens exposed to salt fog and cold were tested with a dynamic mechanical analysis instrument (DMA-983). ASTM D 5023 covers the use of dynamic mechanical instrumentation for gathering viscoelastic properties of thermoplastic and thermosetting resins, as well as composite systems. However, the method exclusively addresses three-point bending techniques. The DMA-983 method uses a two-point bending approach.

In the DMA, the composite samples are slowly heated while undergoing flexural deformation at a fixed frequency and amplitude (no data collected on cooling). The peak of E'' (the loss modulus) in the DMA output can be interpreted as the glass transition temperature (T_g). The T_g is the reversible change in an amorphous polymer, or in amorphous

regions of a partially crystalline polymer from (or to) a viscous or rubbery condition to (or from) a hard and relatively brittle one. For example, as a plastic is gradually heated through a specific temperature range, it changes from a stiff, somewhat brittle material to a more elastic rubbery material. Likewise, when a rubber is cooled to a low temperature, it changes from an elastic material to a solid, hard, somewhat brittle plastic. The flexural modulus E' (as measured at room temperature) will tend to increase, or decrease, from its control value, depending on the type of environment used to weather or age the specimen, as shown in Table 2. For example, E' may increase as the aging process results in further cure from exposure to sunlight (UV). The E' value will likely decrease when plastics are severely heated or exposed to moisture, or both conditions, due to various changes in the polymer chains of the resin (vitrification, hydration and plasticization). Cold (freezing) is expected to have little or no effect because the polymer chains contract during freezing, any further curing of the resin ceases, and the material becomes more impervious to water.

7. RESULTS

The data for flexural strength loss for each composite are summarized in Tables 3 and 4. Data are shown as a reduction in original strength (%) as a function of exposure to each of the environmental conditions. Data for tensile strength loss are summarized in Table 5. This data represents the remaining tensile strength as a function of the original strength, after exposure to each of the conditions.

The flexural strength of the original unexposed samples, and the exposed samples, is also shown in bar charts in Appendix A. Flexural stress versus displacement curves are presented in Appendix B. The numerical values for the tensile strengths are shown in Appendix C.

Data for the DMA testing are presented in Table 6. The parameters for DMA calibration, correlation charts, and sample runs are included in Appendix D.

7.1. Flexural Tests

Flexural data are summarized in Tables 3 and 4, and Table A-1 in Appendix A. The remaining flexural strength values for the weathered composites are reported as a percentage of the control strengths. In some cases increases in flexural strength occurred, attributed to post curing at high temperatures.

Vinylester I

The flexural strength of the vinylester I control was 78,625 psi (Table A-1 in Appendix A). Referring to Table 3, it can be seen that neither dry heat, nor cold, nor UV caused any appreciable strength loss. Exposure to the high oxygen atmosphere, submerging in the salt water in the oxygen atmosphere, or exposure to the salt fog tank, caused flexural strength losses from 13% to 19%. This was the most resistant of all seven GFRP tested.

Vinylester II

The vinylester II also showed little loss in strength from exposure to cold and UV. The initial strength (control) was about 74,724 psi. However, the strengths dropped to the 50,000 psi range for exposures to the oxygen atmosphere, submersion in salt water in the oxygen atmosphere and 12-month exposure in the salt fog tank (24% to 36% loss). The oxygen-rich environments did exhibit some acceleration of the degradation, showing on average 34% losses versus 24% in the salt fog tank. However, this acceleration may not be significant enough to allow for long term durability predictions. Dry heat also caused some weakening of this vinylester (11% loss).

Polyester I

The iso-polyester I exhibited relatively large drops in strength after exposure to oxygen above (28%) and below (22%) the salt water. Surprisingly, exposure in the salt fog tank produced an even greater loss (33%). Strength losses due to exposure to the cold (1%), heat (3%) and UV (0%) were not significant.

Polyester II

The iso-polyester II exhibited strength losses for the oxygen-rich from 23% to 25%, similar to the salt fog tank loss of 25%. Losses from cold temperatures was 16%, and from dry heat 7%. There actually was a very small 1% increase in strength from UV exposure, probably due to further curing.

Phenolic I

Two phenolics were tested. The differences were in the thickness of the strips and the amount of glass roving, as explained in the Background section. For Phenolic I, flexural strength losses were observed after exposure to high oxygen atmosphere (14%), immersion in salt water in high oxygen (33%) and exposure to salt fog (18%). Losses due to exposure to cold (2%) and heat (5%) were not significant. The UV provided further curing and a small strength gain (10%).

Phenolic II

The Phenolic II showed strength losses from the oxygen atmosphere (12%), immersion in salt water in the oxygen tank (57%), and the 12-month salt fog tank (41%). This is the only GFRP that showed significant losses after cold exposure (37%). The flexural strength actually increased 9% after exposure to dry heat and 6% after exposure to UV, which are positive signs of further curing or cross-linking of the polymer resin.

Epoxy-Polyamide

The epoxides of various phenols (such as bis-phenol A or 2,2'– isopropylidene – 4-diphenol) can be reacted with polyamides and polyamines to form "epoxies" with various properties. The epoxy-polyamide composite showed little or no effect from dry heat or UV exposure. The strength seemed to increase less than 1% for the epoxy exposed to the cold. The biggest losses were seen after exposure to the oxygen atmosphere (41%), immersion in salt water in the oxygen atmosphere (43%) and exposure in the salt fog tank (34%).

Results by Exposure Type

From the preceding results, it appears that UV and dry heat did not produce any flexural strength losses, but actually some slight increases due to post-curing. The cold exposure only affected Phenolic II significantly (37% loss), and Polyester II somewhat (16% loss). In some cases, the cold exposure (freezing) actually resulted in a very small increase in stiffness and strength (although part of it is probably due to data scatter). This slight increase has also been reported elsewhere [26].

The main flexural strength losses were due to exposure to seawater, whether in the salt fog chamber, or in an oxygen-rich environment. This is in agreement with previous results by other researchers [18, 19, 20, 24]. On average, the salt fog exposure (at 12 months) resulted in a loss of 27%, the oxygen atmosphere in a loss of 23%, and the oxygen submersion in a loss of 34%. Hence, only the oxygen submersion seemed to exhibit higher decay than the severe natural (tropical) exposure in the salt fog tank. Since the oxygen submersion is a more complex setup, the salt fog exposure is the recommended method for durability assessment.

With respect to the elastic modulus, UV exposure consistently resulted in an increase from the control value (increase from 0% to 14% for all types). Heat and freezing almost always also resulted in a small variation (either small loss or small increase, from –4% to 3%) except for some exceptions (Vinylester II and Phenolic I lost about 10% under heat, Phenolic II lost 34% under cold). The most significant modulus losses were recorded for the Phenolic II (losses from 34% to 40% for oxygen-rich exposure, 12-month salt fog, and cold).

7.2. Tensile Tests

Results of the tensile testing are shown in Table 5 and Appendix C. Since the flexural tests showed that oxygen-rich and salt fog exposures were of most concern, only these exposures were addressed.

The Vinylester I lost little of its strength after being exposed to oxygen atmosphere (15%), oxygen submersion (10%), or salt fog exposure at 28-days (12%). The salt fog exposure at 18 months showed a smaller loss (6%), attributed to data scatter and post-curing.

Vinylester II, on the other hand, lost a considerable amount of strength after exposure to the oxygen-rich environment (30% to 38%). The salt fog exposure at 28 days and 18 months showed losses of only 6% and 8%, respectively.

Polyester I lost a considerable amount of strength in the oxygen-rich environment (27% to 30%) but no loss by exposure to the salt fog for 28 days. Salt fog exposure for 18 months showed a loss of 19%.

Polyester II exhibited a similar behavior, with losses from 19% to 32% for the oxygen-rich environment, but little loss when exposed to the salt fog 28 days. Salt fog exposure for 18 months showed a loss of 12%.

Phenolic I lost 24% of its strength after exposure to the salt fog for 28 days. After 18 months this loss was 28%.

Finally, the epoxy-polyamide exhibited significant losses up to 54% for the oxygen-rich exposures, and 26% for the 28-day salt fog. The 18-month salt fog loss was 39%.

7.3. Thermomechanical Tests (DMA)

DMA data are presented in Table 6 for the control, salt fog, and cold-exposed samples, respectively. Salt fog exposed samples were chosen because the losses observed in the flexural and tensile tests. Samples kept in the freezer were expected to be weakened because of internal damage due to the different thermal expansion coefficients of the fibers and matrix.

Mean values for both starting flexural modulus (E' in GPa units) and glass transition temperatures (peak E'' in °Celsius) were calculated for triplicate samples of each polymer type. The standard deviation and coefficient of variance were also calculated for each mean. Corresponding column charts are given in Figures D-1 and D-2 and include standard deviation bars (± 1 standard deviation) for the mean values of the triplicate samples. Overall, the trends observed between control and exposed flexural modulus values were in agreement with those observed for the MOE (modulus of elasticity) from flexural measurements (see Table A-1). Predicted chemical phenomena for increases and decreases in the flexural modulus and T_g are given in Table 2.

Vinylester I

The starting flexural modulus (mean value) for the vinyl ester I samples was unchanged for both the salt fog and freezer exposures from that of the control samples. This coincides with the results from the flexural tests, in particular for the cold exposure samples (Table 4 or Table A-1).

The T_g mean increased for both the cold and salt fog-exposed samples from that of the controls. This was unexpected for the cold samples since freezing the polymers is expected to stabilize the materials. However, the standard deviation ranges overlapped that of the control's, indicating a lack of significance for these increases.

Vinylester II

The mean flexural storage modulus of both the salt fog and freezer samples remained approximately equal to the control value. This trend was similar to the MOE data from flexural testing, in particular for the freezer samples (Table 4 or Table A-1). Overlapping standard deviations indicate the changes are not significant.

The mean T_g values of both the cold and salt fog-exposed samples remained approximately the same as that of the control samples.

Polyester I

The iso-polyester I exhibited a slight drop (5%) in storage modulus after exposure to salt fog. Flexural testing data also showed a 19% drop under the same exposure (Table 4 or A-1). Exposure to cold resulted in an increase of 9% in the mean modulus over that of the control. This matches the increase of 11% found from the flexural data.

T_g mean values increased slightly for both the salt fog and cold exposures. The T_g standard deviation of the salt fog samples did not overlap that of the controls, indicating possible significance for the salt fog reading. The increase in T_g indicates a stiffer material.

Polyester II

The iso-polyester II exhibited an increase of 15% in flexural storage modulus for the salt fog exposed samples. The cold-exposed modulus remained about the same as the control value. The flexural modulus data from Table 4 (or Table A-1) reveal a small decrease (5%) for either of the exposed samples, in comparison to the controls.

The T_g mean increased over that of the control value for both the salt fog and cold exposures. The lack of overlap between the control and exposed standard deviation ranges suggest these increases may be significant.

Phenolic II

Only Phenolic II was tested by DMA. Results indicate a 6% decrease in the starting flexural modulus for the salt fog exposure, but no change for the freezer exposure. Flexural testing measurements also indicate a higher modulus decrease for salt fog exposure (39%). For the freezer samples, flexural testing measurements indicate a decrease in modulus (34%).

T_g analysis reveals a significant increase for the salt fog samples, and a slight decrease for the freezer samples. Thus the DMA data for flexural modulus is contrary to the T_g data for the salt fog samples. Generally, if the flexural modulus increases, the T_g will also increase and vice-versa.

Epoxy-Polyamide

The starting flexural modulus of the salt fog samples increased by 7% from the control mean. However the standard deviation range still appreciably overlaps that of the control. The modulus mean of the freezer samples decreased (-4%) from the control value, but the standard deviation range is very wide, indicating a lack of significance. Flexural data from Table 4 (or A-1) shows no change for either exposure.

Virtually no change occurred in the T_g values.

Comparison with Other Work

The results of the DMA analyses on salt fog samples are in general agreement with similar studies conducted by NIST (National Institute of Standards and Technology) on vinyl ester and isopolyester films [19]. The NIST study examined molded, thin films of pure resins (230-330 μm thick and no glass fiber reinforcement). Exposure was in 3.5% salt water (1300 hr at room temperature). The NFESC DMA study, on the other hand, was conducted on 3-mm thick composite samples exposed to hot salt fog. Data in the NIST study revealed no significant changes in T_g or E' for the salt-water exposure.

8. CONCLUSIONS

Results indicate that exposure to seawater causes the greatest deterioration of the flexural and tensile strengths of the composites. The salt fog setup provided for an efficient exposure and resulted in significant strength decays. Atmosphere exposure or submersion in an oxygen-rich seawater environment provided little or no deterioration acceleration when

compared to the salt fog exposure. Average flexural strength losses were 27% after 12-month salt fog exposure, 23% for the 12-month oxygen atmosphere exposure, and 34% in the 12-month accelerated oxygen-rich submersion environment. Since the salt fog exposure is a simpler test setup (compared to the oxygen-rich setup), it is recommended for future evaluations.

Tensile tests after salt fog exposures at 28 days and 18 months showed degradations around 10% for vinylesters and polyesters, around 26% for phenolic II, and up to 39% for the epoxy. The oxygen-rich environment did seem to somewhat accelerate the degradation, mostly for the epoxy (54% loss versus 39% at 18 months). Little change was observed in the glass transition temperature, T_g.

Exposure to moderate dry heat, ultraviolet radiation and cold storage in the freezer had little or no effect. Heat and UV radiation actually appeared to further cure some of the composites. Storage in the freezer apparently arrested the curing process but did not embrittle the polymers.

There were statistically different changes in strength for different composites or similar composites from different manufacturers. The details of these changes were analyzed and are reported below for each type of weathering condition.

8.1.   Oxygen-Rich Atmosphere

Photochemical oxidation of polymers causes extensive damage to plastics, rubbers and composites based on these materials. The high oxygen (90-100%) salt-water tank was designed to accelerate the oxidation process that normally takes decades in the field. Vinylester I had the most resistance to oxidation. The epoxy had the least resistance to oxidation, with flexural strength losses of up to 41%. On average, 12-month exposure to the oxygen-rich atmosphere resulted in a flexural degradation similar to that from 12-month exposure to salt fog (while the oxygen submersion showed a slight acceleration). In the tensile tests, the oxygen atmosphere showed a slight acceleration (e.g. 53% loss versus 39% loss for the epoxy at 18 months).

8.2.   Oxygen-Rich Ocean Water Immersion

Vinylester I was again the most resistant to salt water immersion in the presence of 100% oxygen. The phenolics and the epoxy-polyamide are the most susceptible to damage, with flexural strength losses of up to 57%.   Tensile strength losses were up to 54% for the epoxy. The oxygen-rich water immersion resulted in a slight acceleration when compared to the 18-month salt-fog exposure (e.g. 54% loss versus 39% loss for the epoxy).

8.3.   Cold

Samples kept in the freezer at –4ºF for 9 months were expected to be weakened because of damage caused by internal stresses in the material due to the different thermal expansion coefficients of the fibers and matrix. In actual testing, however, there was no

statistically significant change in flexural strength for the composites, except for Phenolic II (37% flexural strength loss) and Polyester II (16% loss).

In terms of the DMA analysis, the lack of significance was expected. As indicated in Table 2, freezing the samples was expected to have little or no effect on the flexural modulus or glass transition temperature of the plastic. Only the Polyester II showed a statistically significant drop in flexural storage modulus.

8.4.   Salt Fog Exposure

Salt fog exposure testing was designed to provide a controlled, high humidity, high temperature (99% humidity and 95°F), corrosive environment. This test has been used extensively to provide relative corrosion or deterioration resistance data. This test differs from the high oxygen-salt water test in that it is performed in 20%-oxygen air. Under salt fog conditions, all of the composites showed strength losses. Vinylester I was the most resistant to degradation by the salt fog exposure. Epoxy and phenolics exhibited the greatest losses in flexural (up to 41%) and tensile strengths (up to 39%).

DMA data indicated that the vinylesters were the most resistant to changes in flexural storage modulus from the salt fog. The greatest loss of flexural modulus appeared to be for Polyester II.

8.5.   Dry Heat

The effect of dry heat (95°F and 50% humidity) on materials is important in operations using composites in a desert region, such as the Persian Gulf. In these tests, only Vinylester II appeared to lose some strength (11%). The remainder of the polymer composites seemed relatively unaffected. It should also be pointed out that some of the flexural test values were slightly above 100% of the control because heat further cures or cross-links polymers that are not completely cured.

8.6.   Ultraviolet Radiation (UV) and Sunlight

Plastics tend to oxidize, crack, and may discolor in the presence of strong sunlight. In the present tests, however, nearly all of the composites retained their strengths. Some of the composites appeared to have strengths slightly in excess of 100% of the controls. This may be due to completion of the cure or cross-linking by the UV.

9. FUTURE WORK

This study was a preliminary phase for testing a limited number of thermoset glass reinforced composites made of polyester, vinylester, phenolic, or epoxy resins. It would be worthwhile to test commercially available glass reinforced thermoplastic composites (polypropylene, polystyrene, nylon, polyvinyl chloride, and others) under the same conditions, for Navy waterfront applications. Many of the thermoplastics are less expensive than the thermoset polymers. Glass reinforced thermoplastic composites (nylon, PVC, and fluorocarbon) were used in NFESC studies on the durability of under-the-pier utility pipe hangers [3]. It would also be of interest to determine strengths after exposure of carbon or graphite reinforced composites made from the same thermoset polymers. Graphite is more expensive than glass, but is generally stronger, more chemically resistant, and more used at the Navy waterfront.

10. ACKNOWLEDGEMENTS

11. REFERENCES

1. Malvar, L.J., editor, "Navy Advanced Composite Technology in Waterfront Infrastructure," SP-2046-SHR, 1997-98 Compendium of Publications, Naval Facilities Engineering Service Center, Port Hueneme, CA, December 1998.

2. Warren, G.E., "Waterfront Repair and Upgrade, Advanced Technology Demonstration Site No. 2: Pier 12, NAVSTA San Diego," Site Specific Report SSR-2419-SHR, Naval Facilities Engineering Service Center, November 1998.

3. Novinson, T., "Polymer Composite Utility Pipe Hangers", Technical Data Sheet, TDS-20250-SHR, Naval Facilities Engineering Service Center, Port Hueneme, CA, March 1996.

4. CALTRANS Division of Structures, "Prequalification Requirements for Alternative Column Casings for Seismic Retrofit (Composites)," California Department of Transportation, 1996.

5. Hawkins, G.F., Steckel, G.L., Bauer, J.L., Sultan, M., "Qualification of Composites for Seismic Retrofit of Bridge Columns," Durability of Fibre Reinforced Polymer (FRP) Composites for Construction, First International Conference on Durability of Composites for Construction, CDCC'98, Sherbrooke, Quebec, Canada, August 1998, pp. 25-36.

6. Steckel, G.L., Hawkins, G.F., Bauer, J.L., "Environmental Durability of Composites for Seismic Retrofit of Bridge Columns," ICCI-98, Second International Conference on Composites in Infrastructure, Tucson, AZ, January 1998, Vol. 2, pp. 460-475.

7. Sultan, M., Hawkins, G., Sheng, L-H., "CALTRANS Program for the Evaluation of Fiber Reinforced Plastics for Seismic Retrofit and Rehabilitation of Structures," Proceedings, FHWA National Seismic Conference, San Diego, CA, 1995.

8. ICBO Evaluation Service, "Acceptance Criteria for Concrete and Reinforced and Unreinforced Masonry, Strengthening using Fibre-Reinforced, Composite Systems," AC125, International Conference of Building Officials, Whittier, CA, 1997.

9. Sonobe, Y., Fukuyama, H., Okamoto, T., Kani, N., Kimura, K., Kobayashi, K., Masuda, Y., Matsuzaki, Y., Mochizuki, S., Nagasaka, T., Shimizu, A., Tanano, H., Tanigaki, M., Teshigawara, M., "Design Guidelines of FRP Reinforced Concrete Building Structures," Journal of Composites for Construction, 1997, Vol. 1, pp. 90-115.

10. Japan Society of Civil Engineers, JSCE, "Recommendation for Design and Construction of Concrete Structures using Continuous Fiber Reinforcing Materials," Concrete Engineering Series, No. 23, Tokyo, 1997, 325 pp.

11. Bakht, B., Al-Bazi, G., Banthia, N., Cheung, M., Erki, M.A., Faoro, M., Machida, A., Mufti, A.A., Neale, K.W., Tadros, G., "Canadian Bridge Design Code provisions for Fiber-Reinforced Structures," Journal of Composites for Construction, Vol. 4, No. 1, February 2000, pp. 3-15.

12. Canadian Standards Association, Canadian Highway Bridge Design Code, Section 16: Fibre Reinforced Structures, and Commentary, 1996, 28 pp.

13. CHBDC Technical Committee 16, "Design Provisions for Fibre Reinforced Structures in the Canadian Highway Bridge Design Code," Advanced Composite Materials in Bridges and Structures, 2nd Intl. Conference, El-Badry ed., Montreal, Quebec, Canada, 1996, pp. 391-406.

14. ACI 440F, "Guide for the Design and Construction of Externally Bonded FRP Systems for Strengthening Concrete Structures," American Concrete Institute Committee 440, 2000.

15. ACI 440H, "Guide for the Design and Construction of Concrete Reinforced with FRP Bars," American Concrete Institute Committee 440, 2000.

16. Reinhart, T.J., editor, "Composites; Engineered Materials Handbook," ASM International, Metals Park, OH, 1987.

17. Malvar, L.J., "Durability of Composites in Concrete," First International Conference on Durability of Composites for Construction, CDCC'98, Sherbrooke, Quebec, Canada, August 1998, pp. 361-372.

18. Karbhari, V.M., Engineer, M., "Effect of Environmental Exposure on the External Strengthening of Concrete with Composites – Short Term Bond Durability," Journal of Reinforced Plastics and Composites, Vol. 15, December 1996, pp. 1194-1216.

19. Chin, J.W., Aouadi, K., Nguyen, T., "Effects of Environmental Exposure on Fiber-reinforced Plastic (FRP) Materials Used in Construction," Journal of Composites Technology & Research, vol. 19, no. 4, 1995, pp. 205-213.

20. Liao, K., Schultheisz, C.R., Hunston, D.L., Brinson, L.C., "Long-Term Durability of Fiber Reinforced Polymer Matrix Composite Materials for Infrastructure Applications: A Review," Journal of Advanced Materials, 1998, Volume 30, No. 4, pp. 3-40.

21. Sen, R., Shahawy, M., Mullins, G., Spain, J., "Durability of Carbon Fiber Reinforced Polymer/Epoxy/Concrete Bond in Marine Environment," ACI Structural Journal, Vol. 96, No. 6, November-December 1999.

22. Tanano, H., Masuda, Y., Tomosawa, F., "Characteristics and Performance Evaluation Methods of Continuous Fiber Bars – State of the Art Studies on Fire Properties and Durability of Continuous Fiber Reinforced Concrete in Japan," Fourth International Symposium on Fiber Reinforced Polymer Reinforcement for Reinforced Concrete Structures, FRPRCS-4, ACI SP-188, Baltimore, MD, October-November 1999, pp. 523-533.

23. Liao, K., Schultheisz, C.R., Hunston, D.L., Brinson, L.C., "Long-Term Durability of Fiber Reinforced Polymer Matrix Composite Materials for Infrastructure Applications: A Review," Journal of Advanced Materials, 1998, Volume 30, pp. 3-40.

24. Dejke, V., "Durability of Fibre Reinforced Polymers (FRP) as Reinforcement in Concrete Structures," Publication P-98:18, Department of building Materials, Chalmers University of Technology, Goteborg, Sweden, February 1999, 69 pp.

25. Tsotis, T.K., "Thermo-Oxidative Aging of Composite Materials," Journal of Composite Materials, vol. 29, no. 3, 1995.

26. Zhang, S., Rivera, J., Karbhari, V., "Investigation of the Effects of Freeze-Thaw Exposure on Composites for Seismic Retrofit," 45th International SAMPE Symposium, Society for the Advancement of Material and Process Engineering, Long Beach, CA, May 2000, pp. 579-593.

TABLE 1. THERMOPLASTIC AND THERMOSET RESINS FOR COMPOSITES

THERMOPLASTICS	THERMOSETS
Acylonitrile-nitrile-styrene polymers (ABS)	Polyesters
Acrylic (e.g. polymethylmethacrylate, PMMA)	Vinylesters
Nylon (also polyamides)	Epoxies
Polycarbonate	Polyurethanes
Polyethylene (HDPE and related materials)	Phenolics
Polypropylene	
Polystyrene	
Polyphenyl sulfide (PPS)	
Polyvinyl chloride (PVC)	
Polyether ketones (PEEK)	

TABLE 2. DMA ANALYSES: PREDICTED TRENDS IN MODULUS AND T_G AFTER EXPOSURE

EXPOSURE CONDITION	FLEXURAL MODULUS E'	GLASS TRANSITION TEMPERATURE T_G
Sunlight (70ºF)	E' increases. The aging process advances the cure of the resin (resin cross-links)	T_g increases
Heat (100ºF)	E' decreases. Vitrification takes place after cure. Sample becomes stiff to the point that it loses flexural strength	T_g decreases
Moisture (80ºF)	E' decreases . The plasticizer effect of moisture on the resin causes hydration of the polymer. Resin will not vitrify. Epoxies are especially susceptible.	T_g decreases
Moisture and Heat (98% RH and 95ºF)	E' decreases. This produces an enhanced plasticizer effect. However, further curing could offset a decrease.	T_g decreases (if initially fully cured)
Freezing (-4ºF)	The molecular structure of the resin contracts (while at –4ºF.) and prevents the resin from further curing. The resin becomes impervious to water absorption.	No effect on T_g

TABLE 3. REMAINING FLEXURAL STRENGTH AFTER EXPOSURE (% OF ORIGINAL STRENGTH)

Material	Oxygen Atmosphere	Oxygen Submersion	Cold	Salt Fog 28 days	Salt Fog 1 year	Heat *	UV *
Vinylester I	87%	81%	101%	104%	86%	100%	97%
Vinylester II	68%	64%	98%	96%	76%	89%	97%
Polyester I	72%	78%	99%	88%	67%	97%	100%
Polyester II	77%	75%	84%	87%	75%	93%	101%
Phenolic I	86%	67%	98%	102%	82%	95%	110%
Phenolic II	88%	43%	63%	77%	59%	109%	106%
Epoxy-amide	59%	57%	101%	76%	66%	98%	98%

* values higher than 100% due to post curing

TABLE 4. ELASTIC MODULUS AFTER EXPOSURE (% OF ORIGINAL STRENGTH)

Material	Oxygen Atmosphere	Oxygen Submersion	Cold	Salt Fog 28 days	Salt Fog 1 year	Heat *	UV *
Vinylester I	88%	87%	100%	103%	91%	99%	100%
Vinylester II	99%	85%	98%	98%	90%	90%	108%
Polyester I	95%	96%	111%	92%	81%	99%	101%
Polyester II	83%	95%	96%	95%	95%	96%	107%
Phenolic I	101%	90%	100%	112%	94%	91%	102%
Phenolic II	65%	60%	66%	90%	61%	103%	114%
Epoxy-amide	99%	92%	101%	106%	100%	100%	103%

* values higher than 100% due to post curing

TABLE 5. REMAINING TENSILE STRENGTH AFTER EXPOSURE (AS A % OF ORIGINAL STRENGTH)

Material	Oxygen Atmosphere	Oxygen Submersion	Salt Fog 28 days	Salt Fog 18 months
Vinylester I	85%	90%	88%	94%
Vinylester II	62%	70%	94%	92%
Polyester I	70%	73%	99%	81%
Polyester II	81%	68%	95%	88%
Phenolic I	N/A	N/A	76%	72%
Epoxy-amide	47%	46%	74%	61%

TABLE 6.   DMA FLEXURAL MODULUS E' (GPA) AND GLASS TRANSITION
TEMPERATURE T$_G$ (PEAK E" IN DEGREES CELSIUS)

Polymer	Exposure	Sample	Start E'	Repl Mean	Std Dev	CV %	Peak E"	Repl Mean	Std Dev	CV %
Vinyl I	Control	A005.2	16.66				108			
Vinyl I	Control	A008.1	19.43	17.9	1.4	7.8	110.6	109.2	1.3	1.2
Vinyl I	Control	A006.2	17.64				108.9			
Vinyl I	Salt Fog	A029	16.53				108.3			
Vinyl I	Salt Fog	A035	18.84	17.8	1.2	6.6	117	111.9	4.5	4.1
Vinyl I	Salt Fog	A038	18.12				110.4			
Vinyl I	Freezer	A024	18.14				113.6			
Vinyl I	Freezer	A025	18.29	17.9	0.5	2.7	125.6	117.0	7.5	6.4
Vinyl I	Freezer	A033	17.38				111.7			
Vinyl II	Control	B007.1	16.71				108			
Vinyl II	Control	B008.1	17.93	17.2	0.6	3.6	106.6	107.0	0.9	0.8
Vinyl II	Control	B010.1	17.08				106.4			
Vinyl II	Salt Fog	B034	17.13				105.6			
Vinyl II	Salt Fog	B036	18.55	17.6	0.8	4.8	108.3	107.2	1.4	1.3
Vinyl II	Salt Fog	B038	17.07				107.6			
Vinyl II	Freezer	B032	16.83				109.7			
Vinyl II	Freezer	B037	16.74	16.7	0.2	1.0	107.2	109.0	1.5	1.4
Vinyl II	Freezer	B047	16.51				110			
Polyester I	Control	C006.2	17.02				90.92			
Polyester I	Control	C007.1	16.69	17.1	0.5	2.7	90.15	91.2	1.3	1.4
Polyester I	Control	C009.1	17.6				92.63			
Polyester I	Salt Fog	C024	17.1				97.04			
Polyester I	Salt Fog	C026	16.45	16.2	1.1	6.9	95.42	95.7	1.2	1.3
Polyester I	Salt Fog	C030	14.93				94.63			
Polyester I	Freezer	C028	18.08				92.78			
Polyester I	Freezer	C033	18.66	18.6	0.5	2.9	93.7	93.6	0.8	0.9
Polyester I	Freezer	C035	19.17				94.4			
Polyester II	Control	D006.1	14.99				95.98			
Polyester II	Control	D009.1	16.45	16.3	1.3	8.0	98.35	97.5	1.3	1.3
Polyester II	Control	D010.1	17.59				98.08			
Polyester II	Salt Fog	D024	17.13				102.2			
Polyester II	Salt Fog	D031	19.49	18.8	1.5	7.9	106.8	103.6	2.7	2.7
Polyester II	Salt Fog	D035	19.86				101.9			
Polyester II	Freezer	D034	14.52				105			
Polyester II	Freezer	D038	16.65	16.3	1.6	9.8	99.72	104.8	5.0	4.8
Polyester II	Freezer	D039	17.66				109.7			
Epoxy	Control	F006.2	17.91				153.9			
Epoxy	Control	F009.1	20.6	19.9	1.7	8.8	149.6	152.1	2.2	1.5
Epoxy	Control	F010.1	21.19				152.7			
Epoxy	Salt Fog	F036	21.61				153.1			
Epoxy	Salt Fog	F039	20.6				155.9			
Epoxy	Salt Fog	F037	21.64	21.3	0.6	2.8	152.3	153.8	1.9	1.2
Epoxy	Freezer	F025	16.54				155.6			
Epoxy	Freezer	F028	18.7				151.5			
Epoxy	Freezer	F038	22.1	19.1	2.8	14.7	157.8	155.0	3.2	2.1
Phenolic II	Control	E008.1	9.36				171.8			
Phenolic II	Control	E010.1	8.3				173.6			
Phenolic II	Control	E009.1	11.3	9.7	1.5	15.8	166.5	170.6	3.7	2.2
Phenolic II	Salt Fog	E025	10.69				186.2			
Phenolic II	Salt Fog	E042	9.529				176.3			
Phenolic II	Salt Fog	E061	6.948	9.1	1.9	21.2	187	183.2	6.0	3.3
Phenolic II	Freezer	E031	11.51				157.9			
Phenolic II	Freezer	E042	9.456				174.6			
Phenolic II	Freezer	E061	7.906	9.6	1.8	18.8	167.9	166.8	8.4	5.0
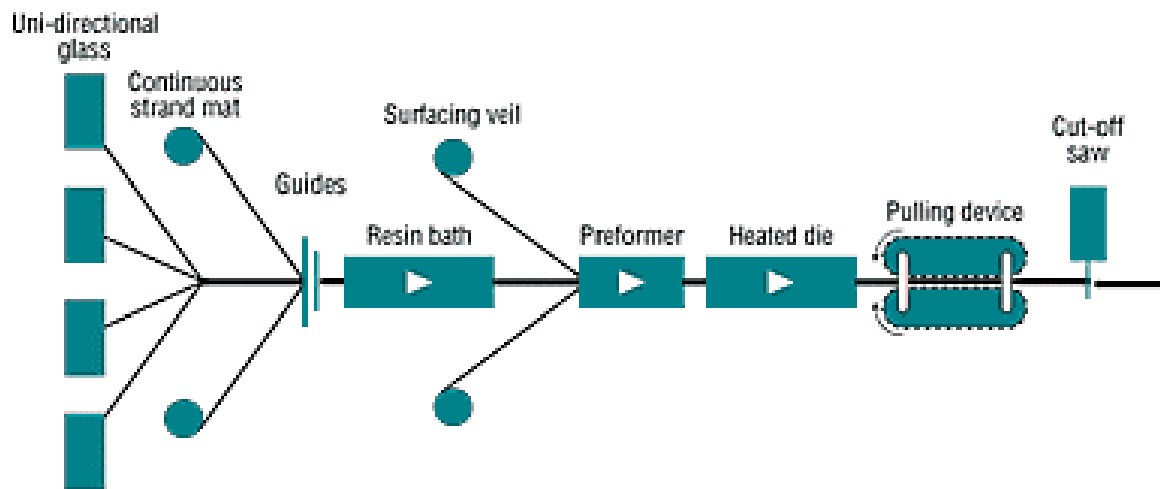
FIGURE 1. PULTRUSION PROCESS SCHEMATIC
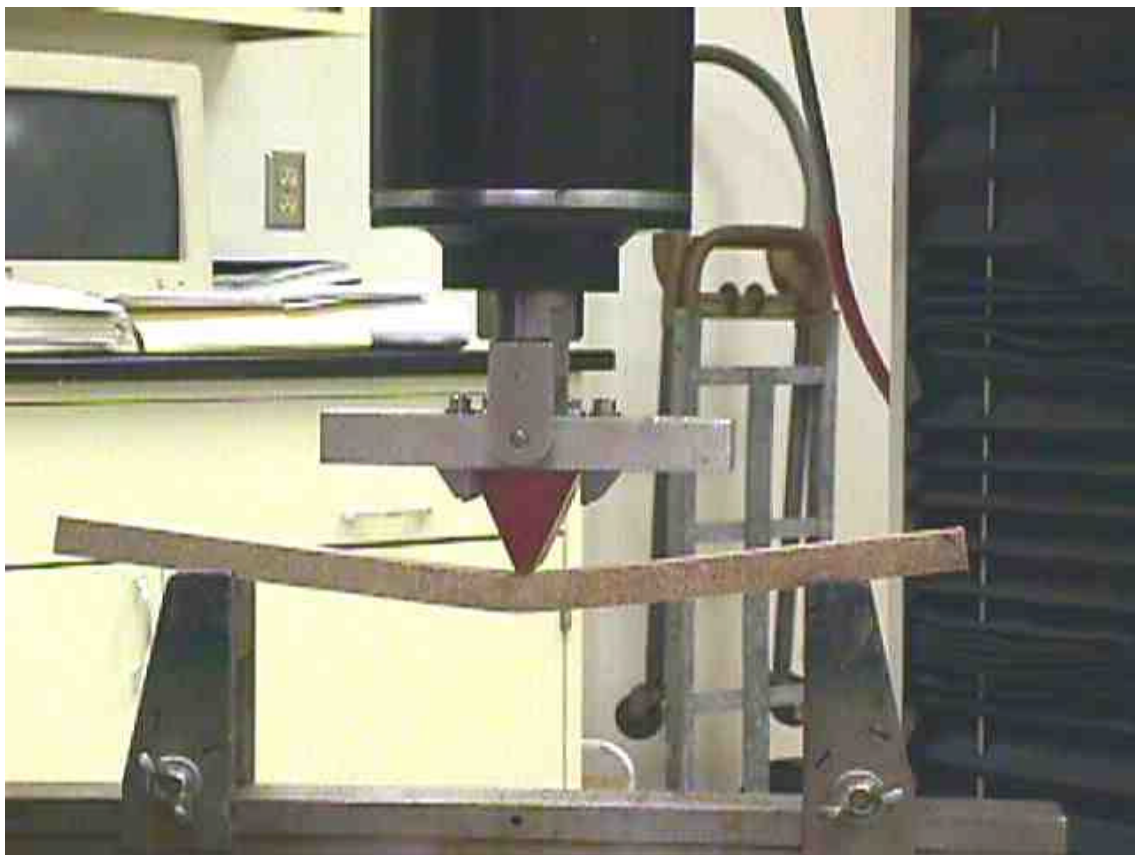
FIGURE 2. TEST APPARATUS FOR FLEXURAL TESTING (ASTM D790)

22
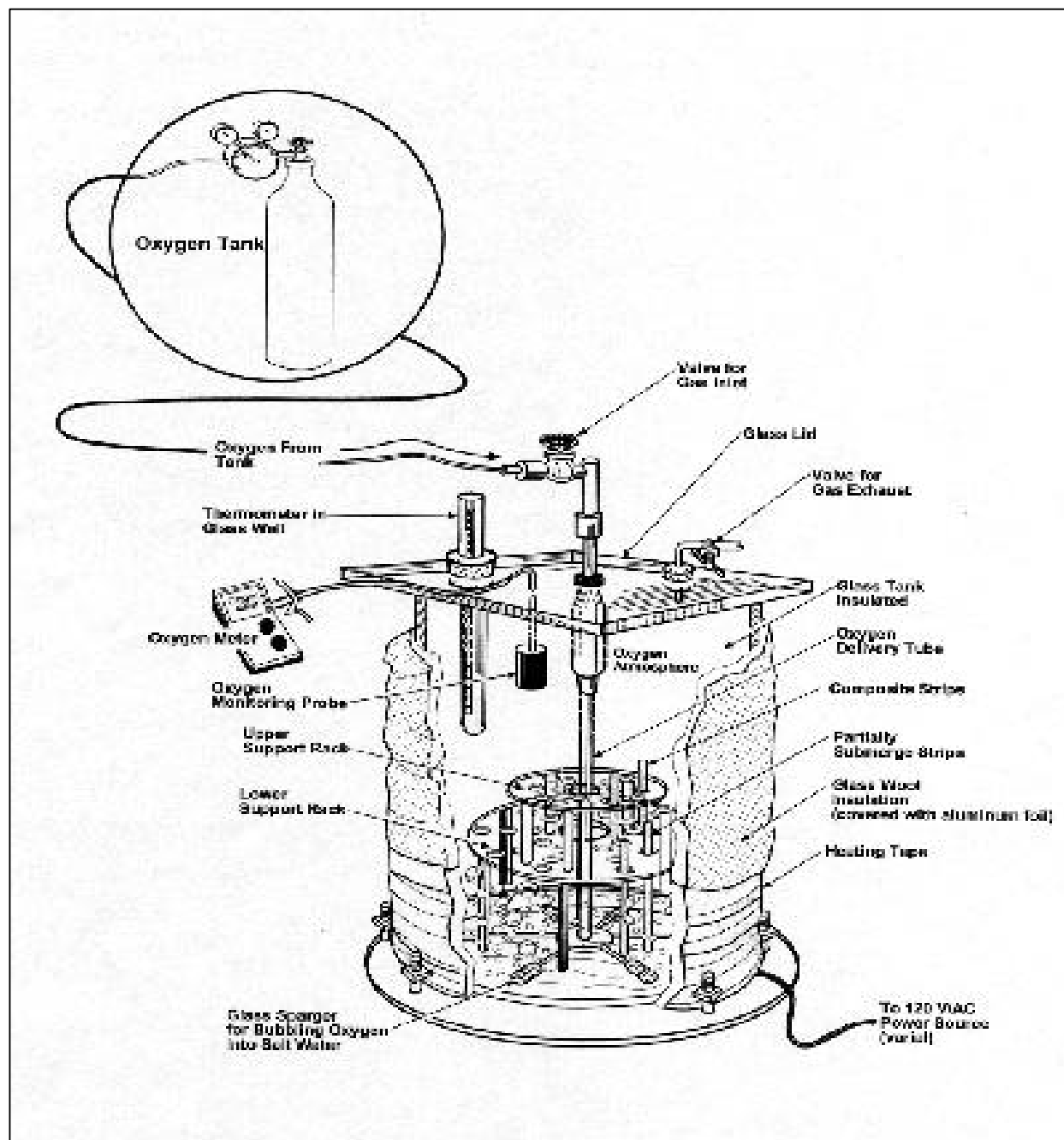
FIGURE 3. HIGH OXYGEN SALT WATER SYSTEM

FIGURE 4. SALT FOG CHAMBER

FIGURE 5. HEAT EXPOSURE TEST

FIGURE 6. UV EXPOSURE APPARATUS
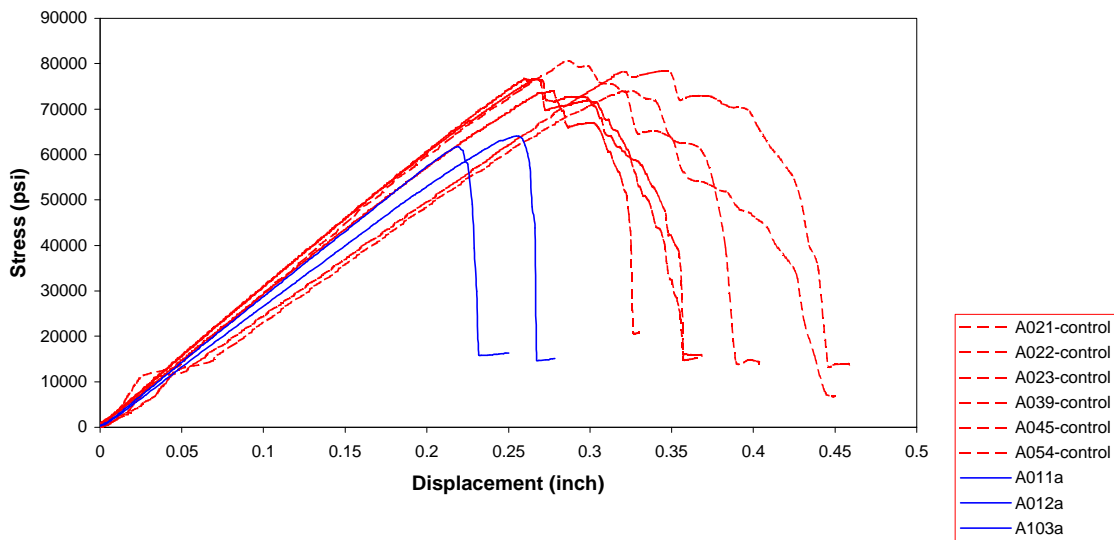
APPENDIX A – SUMMARY OF FLEXURAL STRENGTH DATA

This appendix includes the flexural strength data for both controls and weathered specimens. In the following graphs, the nomenclature is as follows:

(1) Control specimen – CONTROL
(2) Oxygen (100%) and salt water spray (100ºF) for 12 months – OXYGEN ATMOSPHERE
(3) Oxygen (100%) and salt water submersion (100ºF) 12 months – OXYGEN SUBMERSION
(4) Cold freezer (-4ºF) for 9 months – COLD
(5) Salt fog tank (95ºF) for 12 months – SALT FOG
(6) Dry heat oven (95ºF) for 120 days – HEAT
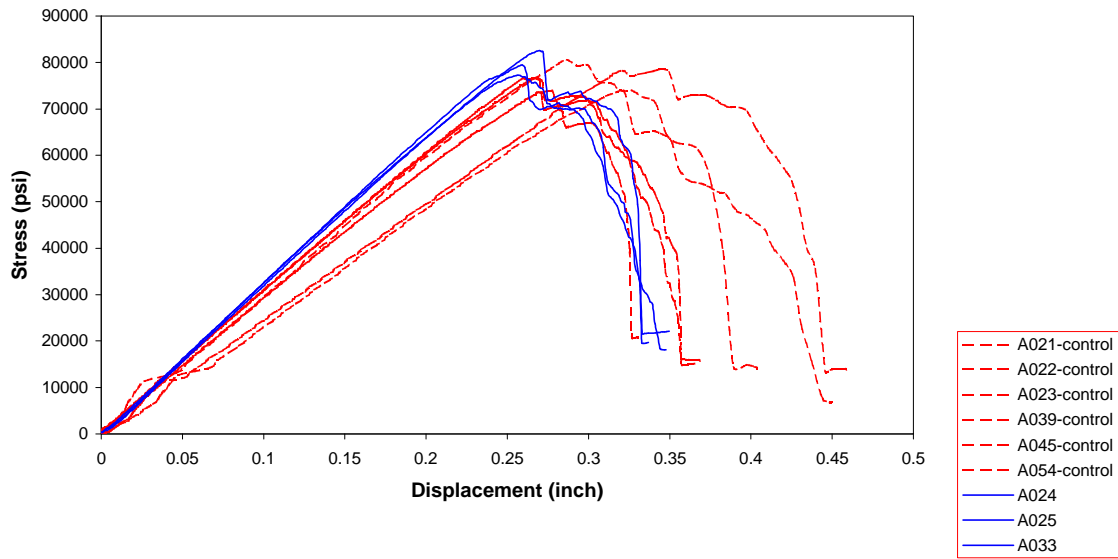(7) Ultraviolet exposure unit (70ºC or 158ºF cycles) for 90 days – UV
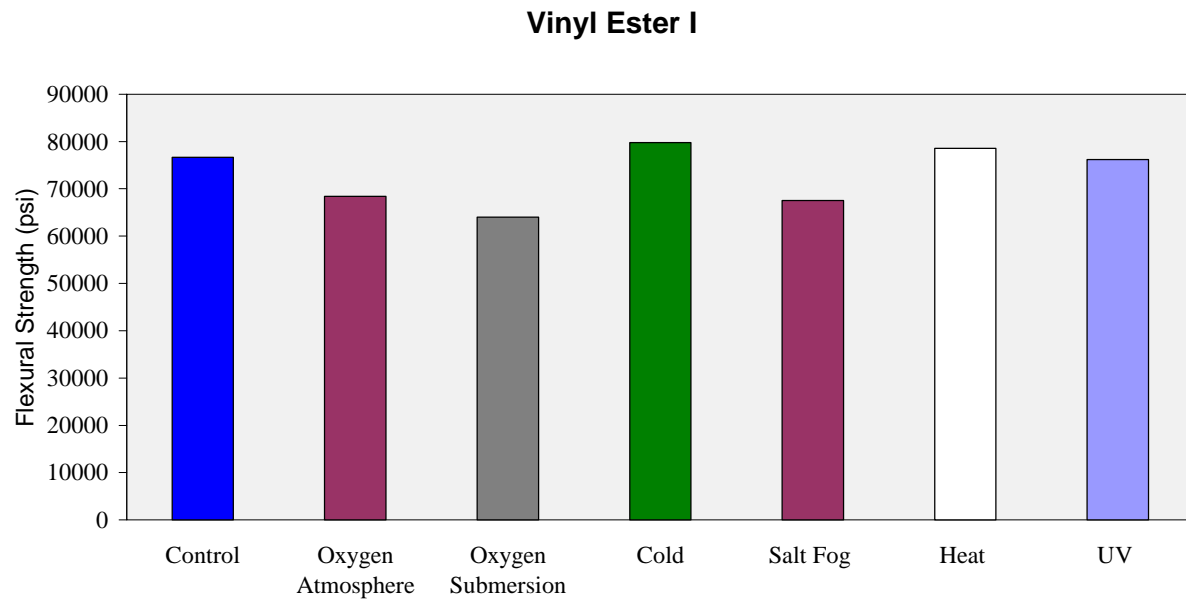
Vinyl Ester I

FIGURE A-1. FLEXURAL STRENGTH FOR VINYLESTER I.
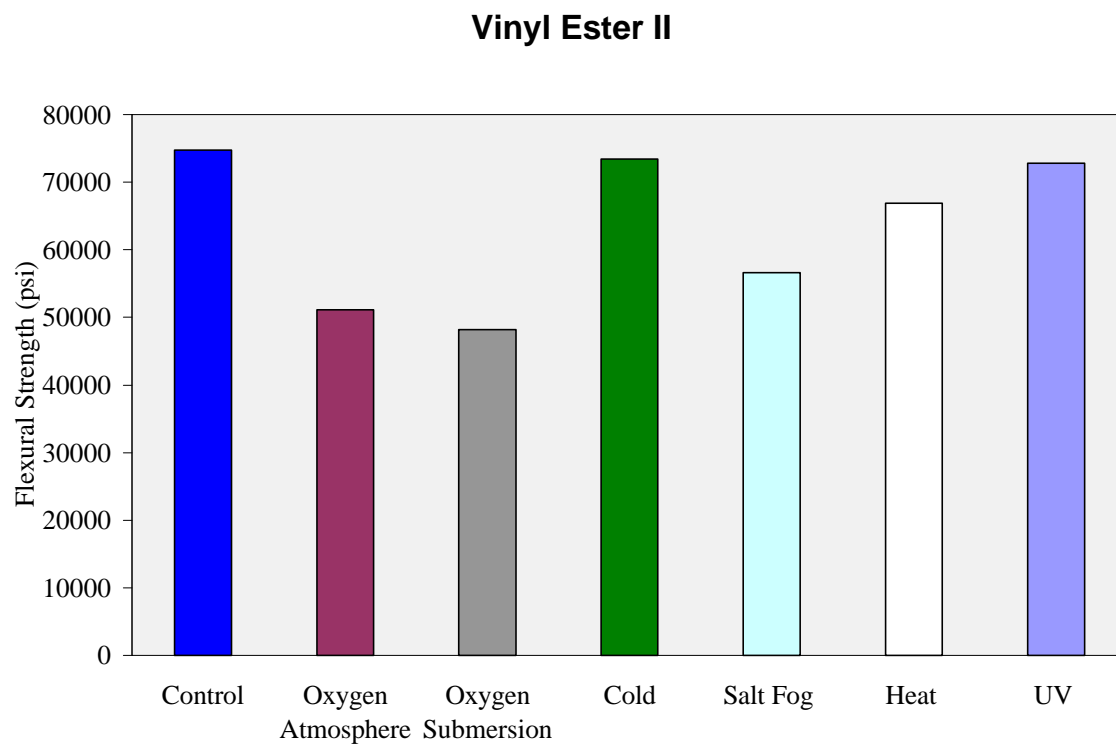
Vinyl Ester II

FIGURE A-2. FLEXURAL STRENGTH FOR VINYLESTER II.

Iso Polyester I
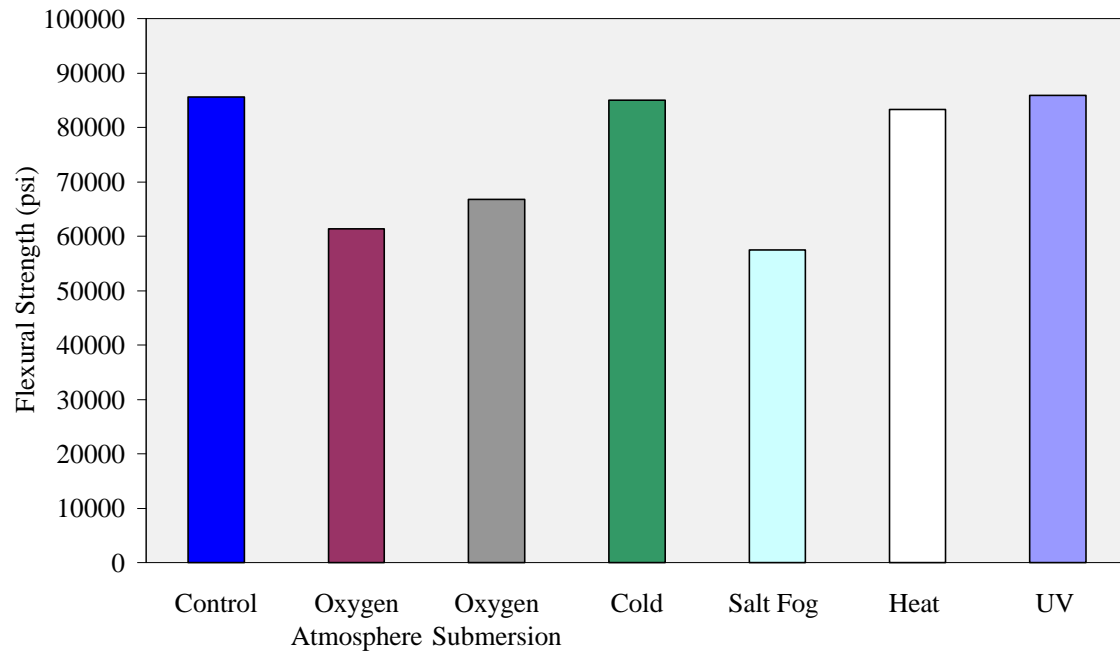
FIGURE A-3. FLEXURAL STRENGTH FOR POLYESTER I.

Iso Polyester II
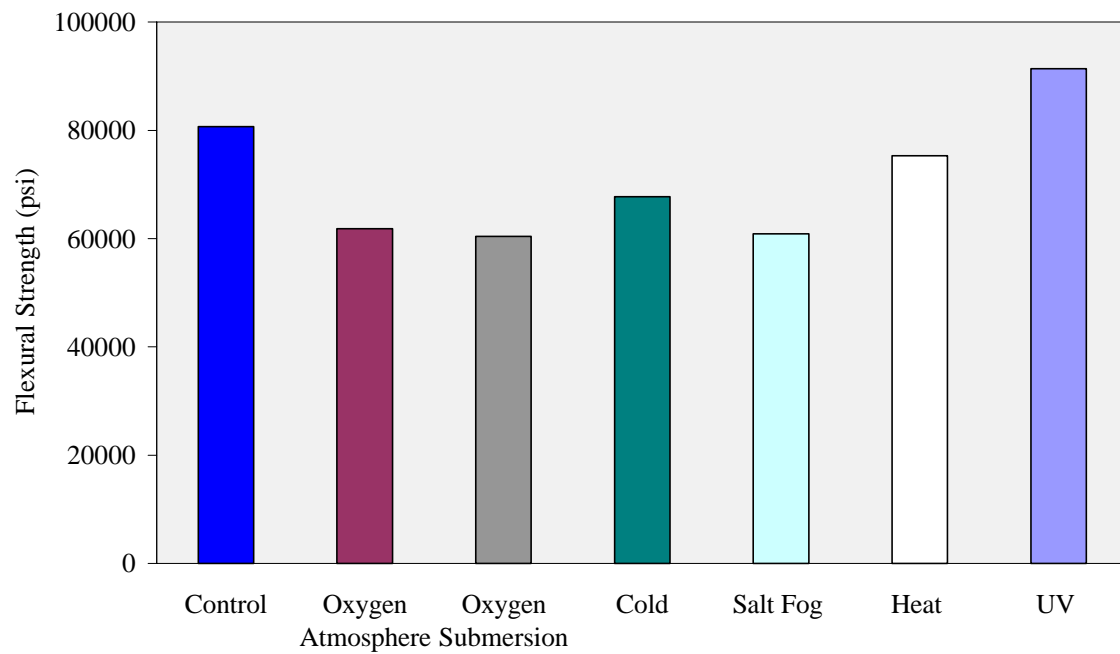
FIGURE A-4. FLEXURAL STRENGTH FOR POLYESTER II.

Phenolic I
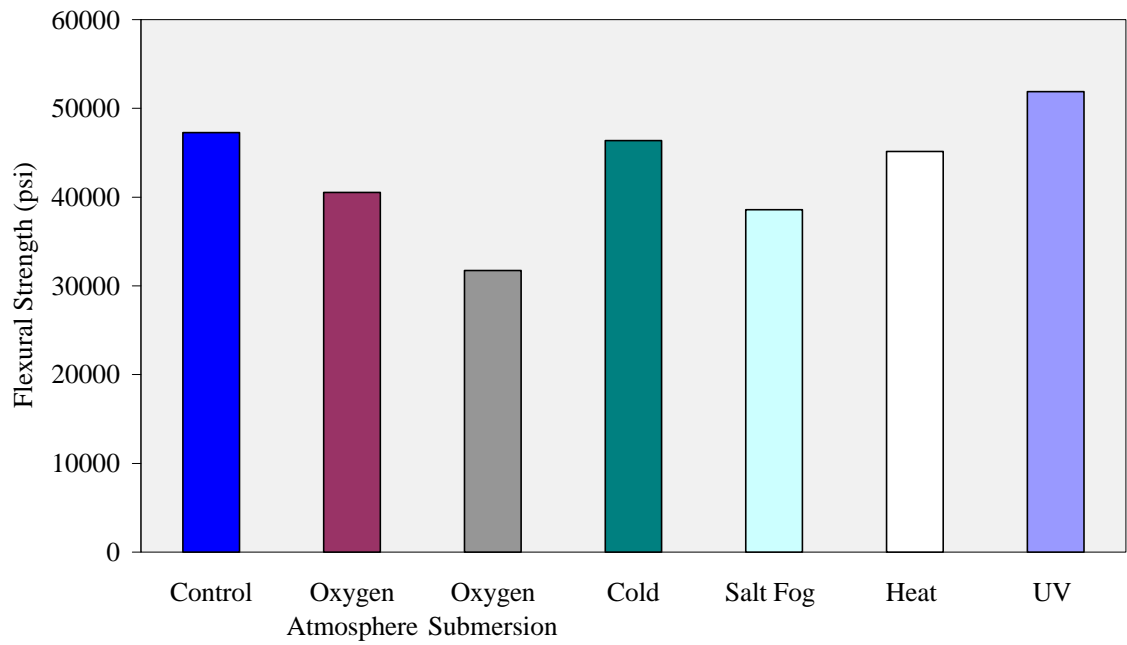
FIGURE A-5. FLEXURAL STRENGTH FOR PHENOLIC I.

Phenolic II
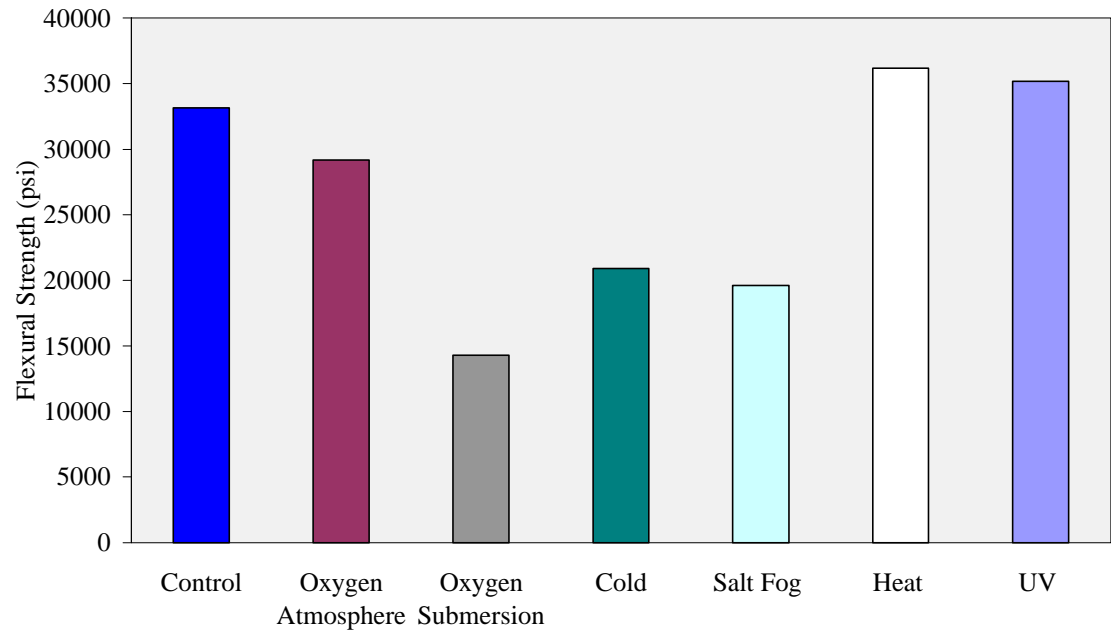
FIGURE A-6. FLEXURAL STRENGTH FOR PHENOLIC II.
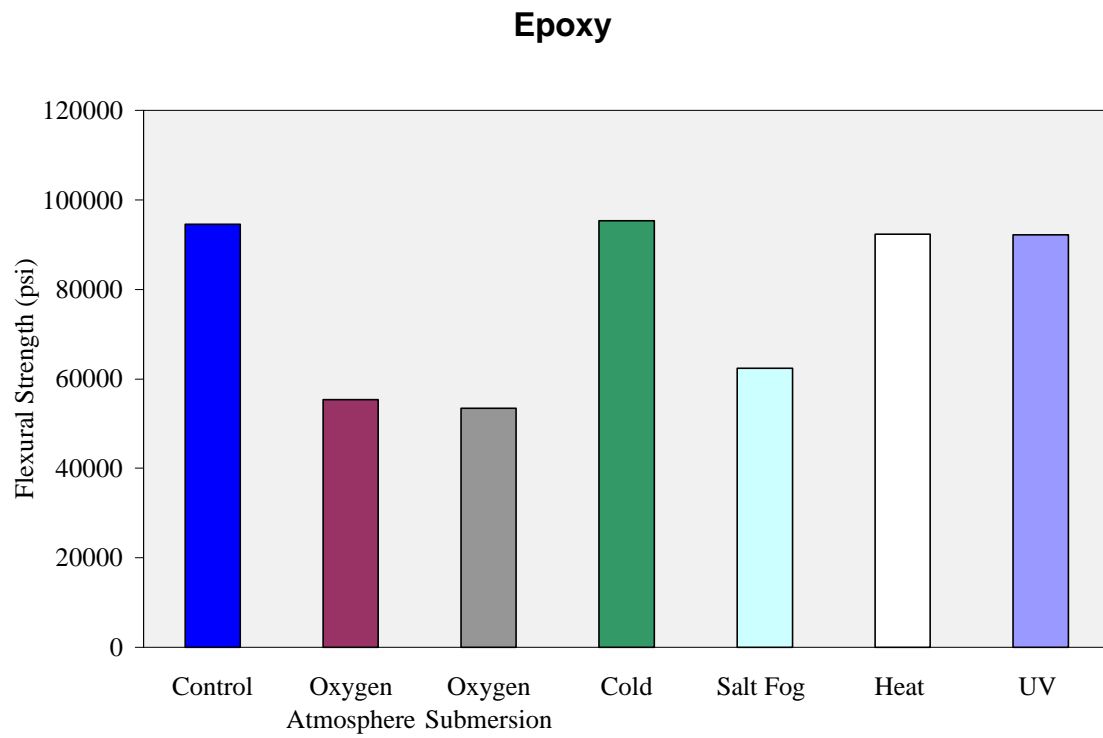
Epoxy

FIGURE A-7. FLEXURAL STRENGTH FOR EPOXY.

TABLE A-1. SUMMARY OF FLEXURAL TESTING DATA

Vinyl Ester I Exposure	Ult Stress psi	Displacement inch	Modulus of elasticity Ksi
Control	78625	0.294	2678
Oxy Atmosphere	68451	0.256	2362
Oxy Submersion	63996	0.235	2319
Cold	79786	0.262	2680
Salt Fog 28 days	81775	0.255	2757
Salt Fog 1 year	67578	0.251	2446
Heat	78553	0.258	2640
UV	76235	0.250	2680
Vinyl Ester II Exposure	**Ult Stress psi**	**Displacement inch**	**Modulus of elasticity Ksi**
Control	74724	0.284	2425
Oxy Atmosphere	51114	0.182	2403
Oxy Submersion	48181	0.203	2057
Cold	73416	0.274	2388
Salt Fog 28 days	72023	0.259	2383
Salt Fog 1 year	56616	0.231	2187
Heat	66874	0.264	2180
UV	72843	0.247	2608
Iso Polyester I Exposure	**Ult Stress psi**	**Displacement inch**	**Modulus of elasticity Ksi**
Control	85541	0.330	2357
Oxy Atmosphere	61345	0.236	2240
Oxy Submersion	66750	0.260	2255
Cold	84963	0.294	2621
Salt Fog 28 days	75457	0.292	2168
Salt Fog 1 year	57455	0.272	1907
Heat	83256	0.307	2324
UV	85889	0.319	2377
Iso Polyester II Exposure	**Ult Stress psi**	**Displacement inch**	**Modulus of elasticity Ksi**
Control	80651	0.327	2254
Oxy Atmosphere	61844	0.264	1860
Oxy Submersion	60386	0.252	2147
Cold	67770	0.286	2174
Salt Fog 28 days	70080	0.276	2151
Salt Fog 1 year	60865	0.260	2147
Heat	75307	0.308	2157
UV	81632	0.298	2408

TABLE A-1. SUMMARY OF FLEXURAL TESTING DATA (CONTINUED)

Phenolic I Exposure	Ult Stress psi	Displacement inch	Modulus of elasticity Ksi
Control	47292	0.362	1995
Oxy Atmosphere	40532	0.330	2006
Oxy Submersion	31724	0.237	1799
Cold	46371	0.373	2001
Salt Fog 28 days	48272	0.227	2238
Salt Fog 1 year	38575	0.377	1879
Heat	45146	0.400	1824
UV	51874	0.401	2039

Phenolic II Exposure	Ult Stress psi	Displacement inch	Modulus of elasticity Ksi
Control	33155	0.153	1748
Oxy Atmosphere	29164	0.140	1128
Oxy Submersion	14287	0.116	1051
Cold	20897	0.127	1159
Salt Fog 28 days	25364	0.366	1573
Salt Fog 1 year	19608	0.280	1058
Heat	36170	0.173	1801
UV	35167	0.140	1988

Epoxy Exposure	Ult Stress psi	Displacement inch	Modulus of elasticity Ksi
Control	94520	0.316	2861
Oxy Atmosphere	55317	0.161	2846
Oxy Submersion	53495	0.166	2634
Cold	95370	0.297	2888
Salt Fog 28 days	72073	0.196	3024
Salt Fog 1 year	62358	0.184	2850
Heat	92316	0.285	2863
UV	92120	0.283	2943

APPENDIX B – COMPLETE FLEXURAL STRENGTH DATA

This appendix includes the flexural strength data for both controls and weathered specimens. In the following graphs, the nomenclature is as follows:

(1) Control specimen – CONTROL
(2) Oxygen (100%) and salt water spray (100ºF) for 12 months – OCEAN ATMOSPHERE
(3) Oxygen (100%) and salt water immersion (100ºF) for 12 months – OCEAN SUBMERSION
(4) Cold freezer (-4ºF) for 9 months – COLD
(5) Salt fog tank (95ºF) for 12 months – SALT FOG
(6) Dry heat oven (95ºF) for 120 days – HEAT
(7) Ultraviolet exposure unit (70ºC or 158ºF cycles) for 90 days – UV

Stress vs Displacement
Vinyl Ester I
Oxygen Atmosphere Exposure and Controls

Legend:
- A021-control
- A022-control
- A023-control
- A039-control
- A045-control
- A054-control
- A017
- A018
- A020
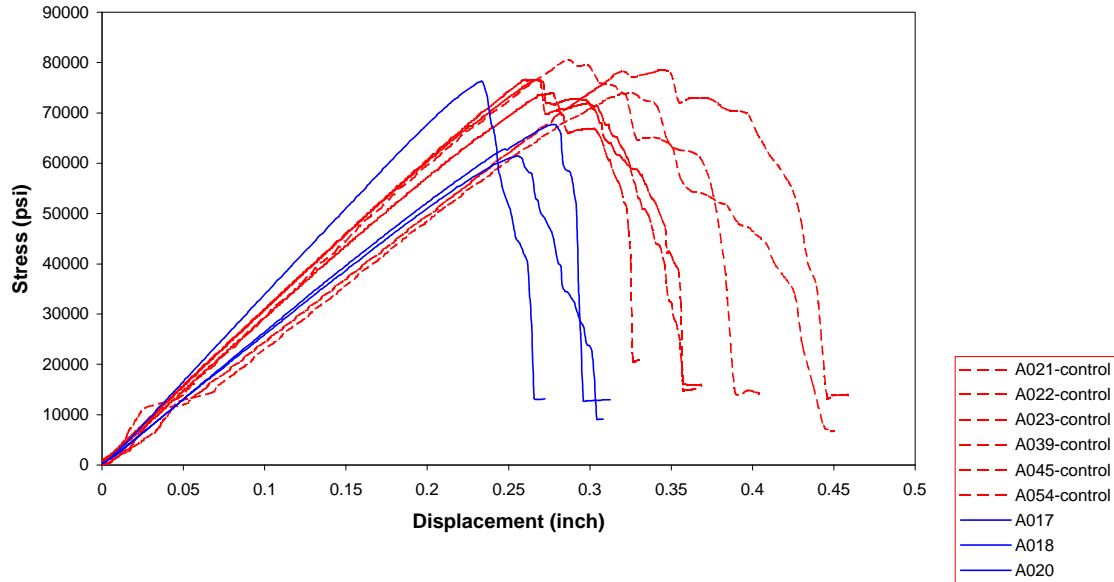
Stress vs Displacement
Vinyl Ester I
Oxygen/Submersion Exposure and Controls

Legend:
- A021-control
- A022-control
- A023-control
- A039-control
- A045-control
- A054-control
- A011a
- A012a
- A103a

Stress vs Displacement
Vinyl Ester I
Cold Exposure and Controls

Legend:
A021-control
A022-control
A023-control
A039-control
A045-control
A054-control
A024
A025
A033

Stress vs Displacement
Vinyl Ester I
Salt Fog Exposure and Controls

Legend:
A021-control
A022-control
A023-control
A039-control
A045-control
A054-control
A029
A035
A038
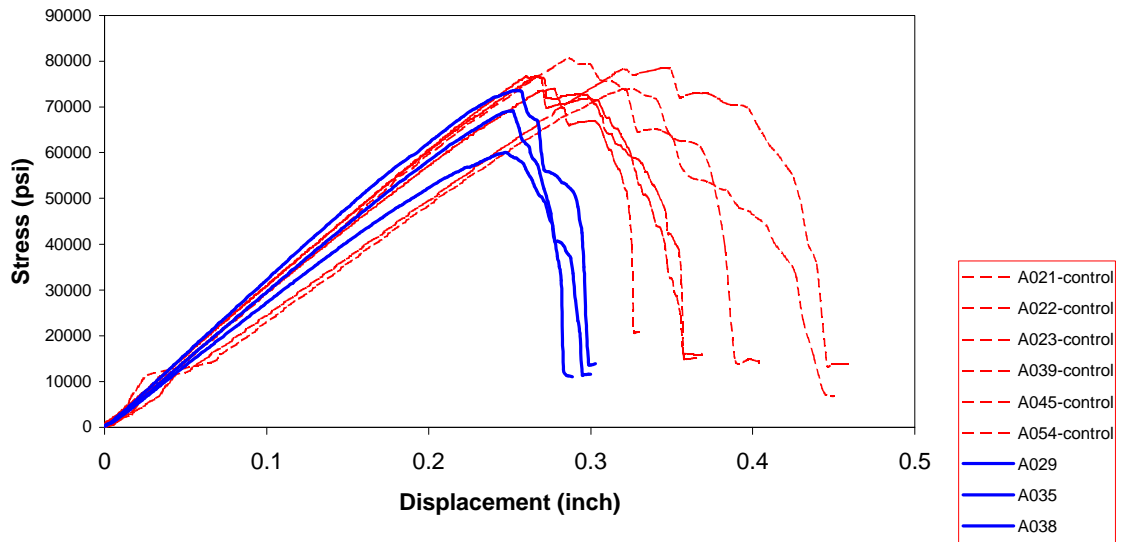
Stress vs Displacement
Vinyl Ester I
Heat Exposure and Controls
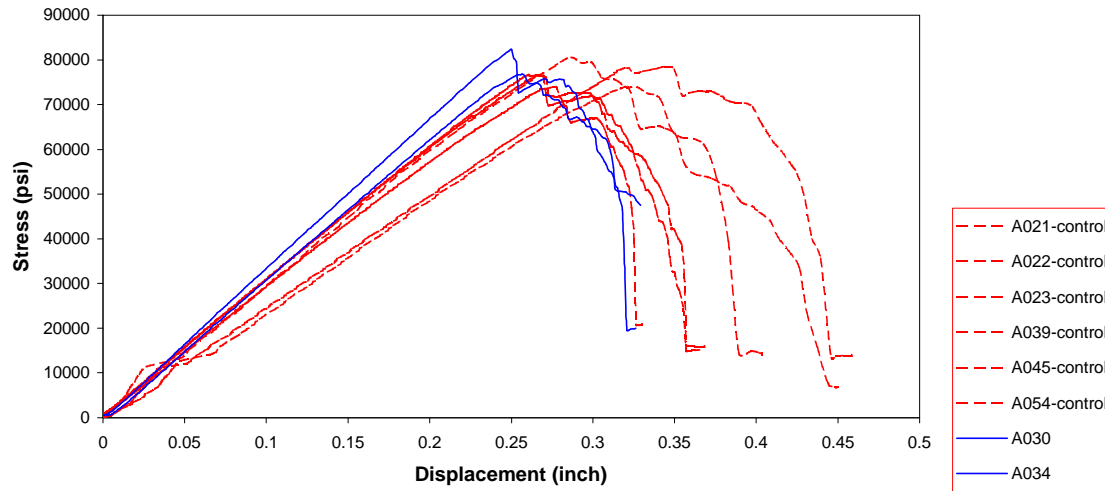
Stress vs Displacement
Vinyl Ester I
UV Exposure and Controls
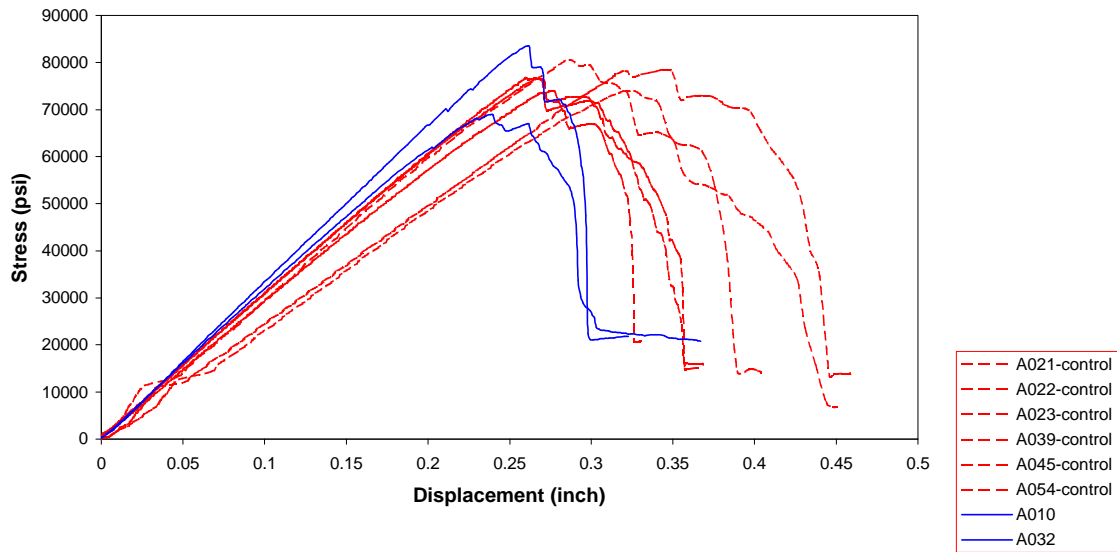
Stress vs Displacement
Vinyl Ester II
Oxygen Atmosphere Exposure and Controls
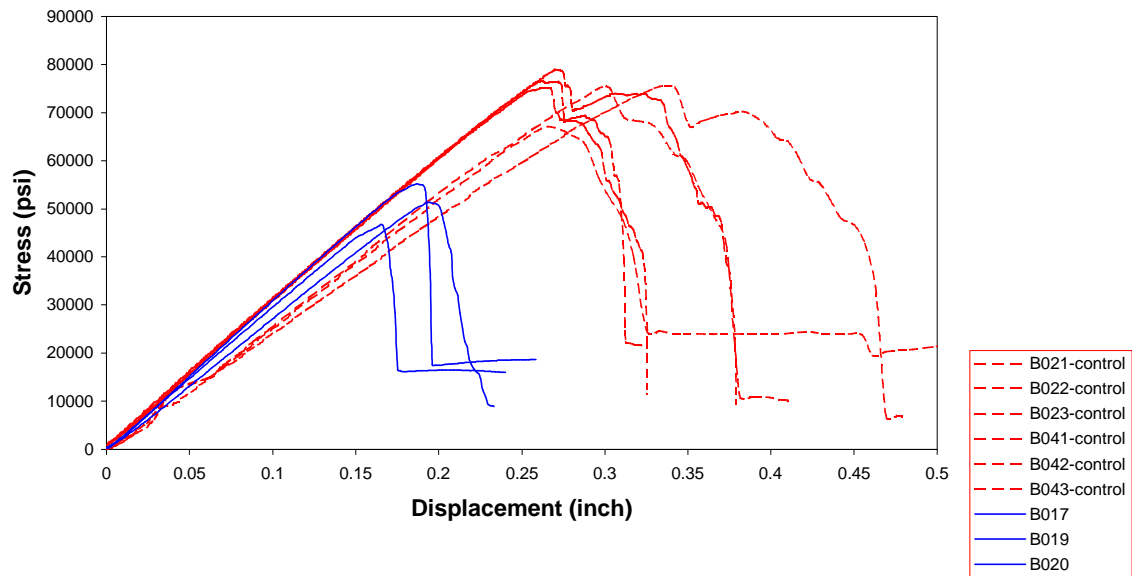
Stress vs Displacement
Vinyl Ester II
Oxygen Submersion Exposure and Controls
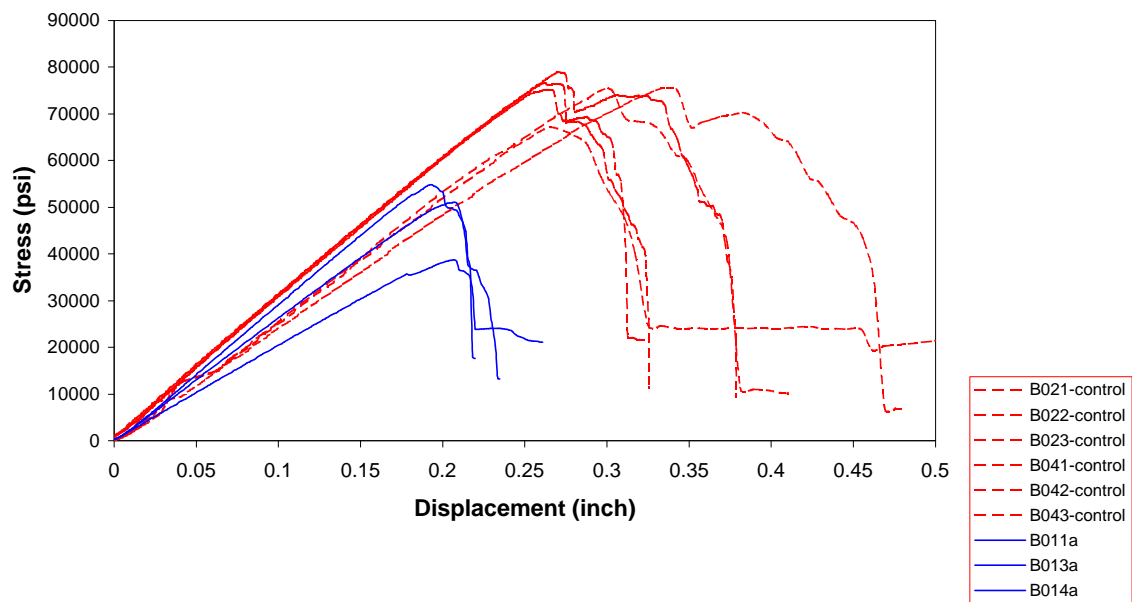
Stress vs Displacement
Vinyl Ester II
Cold Exposure and Controls
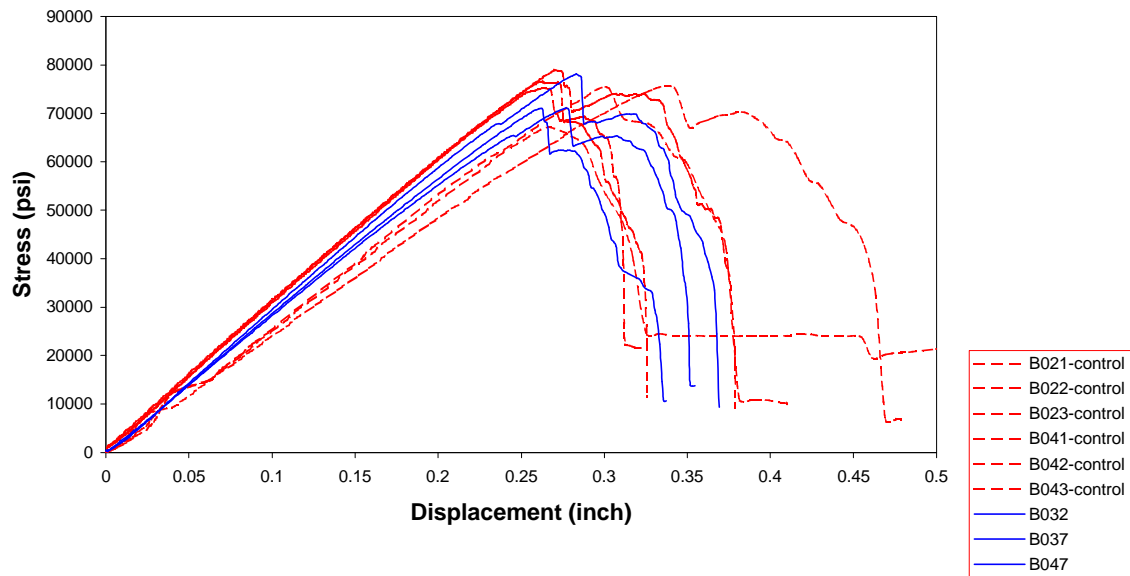
Stress vs Displacement
Vinyl Ester II
Salt Fog Exposure and Controls
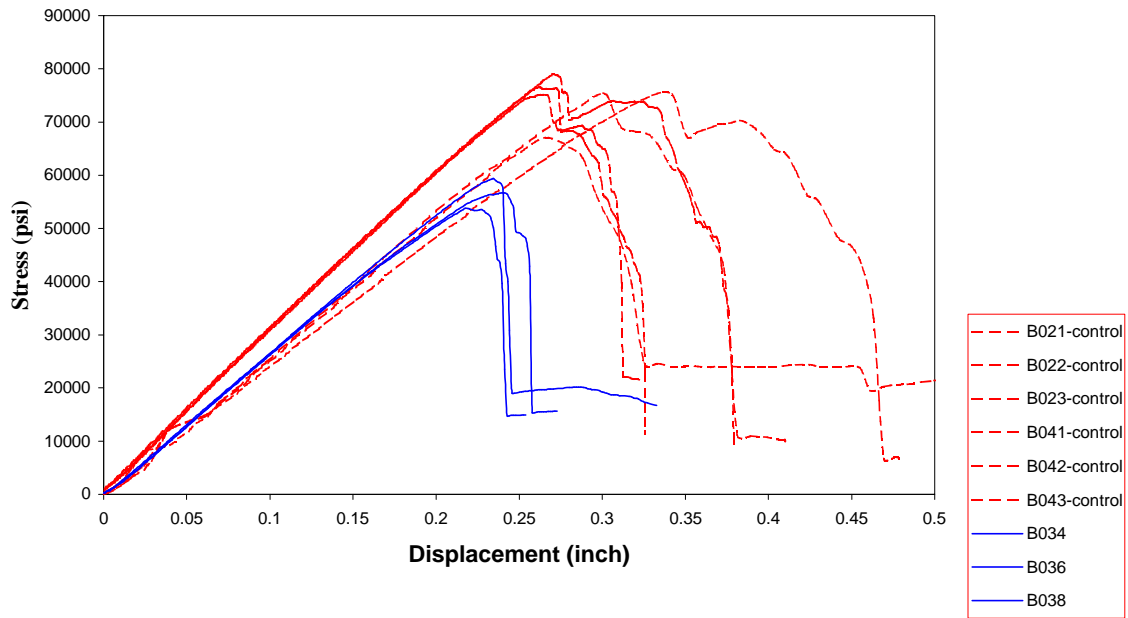
Stress vs Displacement
Vinyl Ester II
Heat Exposure and Controls

Legend:
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- B022-control
- B023-control
- B041-control
- B042-control
- B043-control
- B025
- B027
- B29
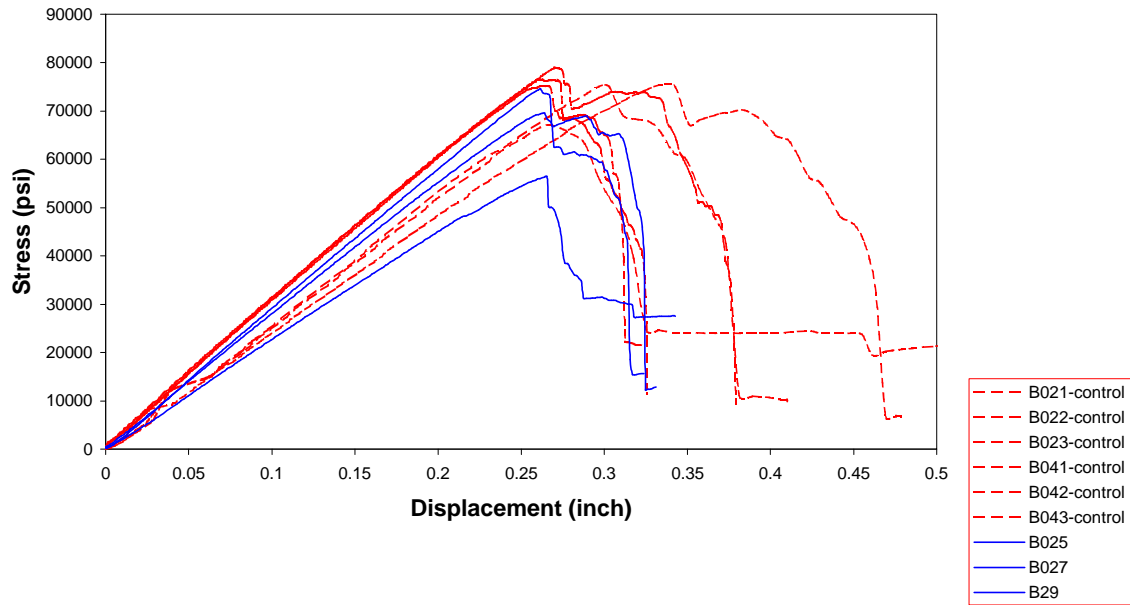
Stress vs Displacement
Vinyl Ester II
UV Exposure and Controls

Legend:
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- B022-control
- B023-control
- B041-control
- B042-control
- B043-control
- B031
- B033
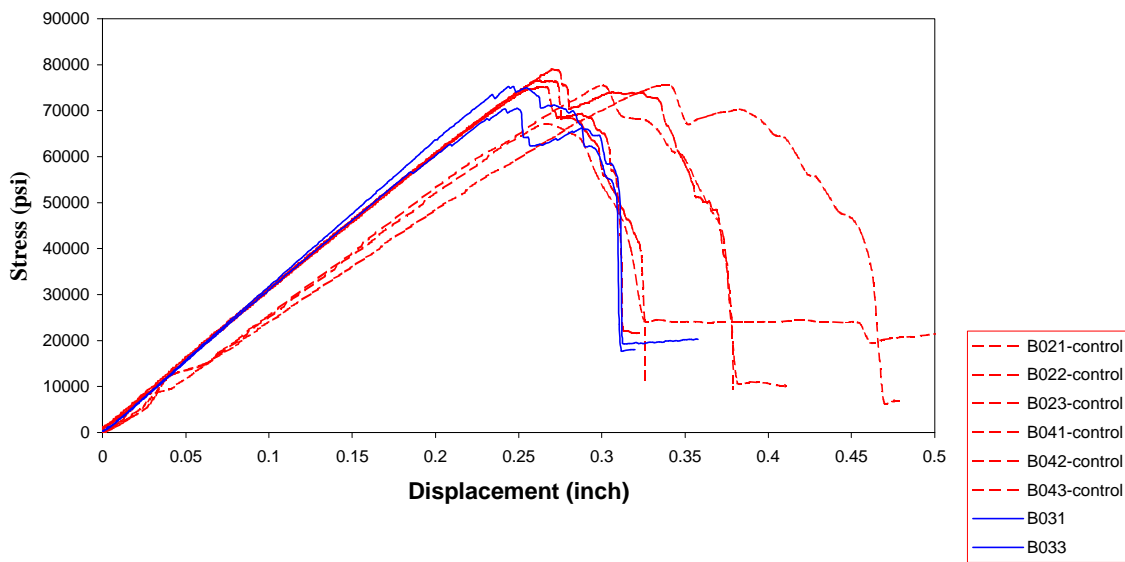
Stress vs Displacement
Iso Polyester 1
Ocean Atmosphere Exposure and Controls
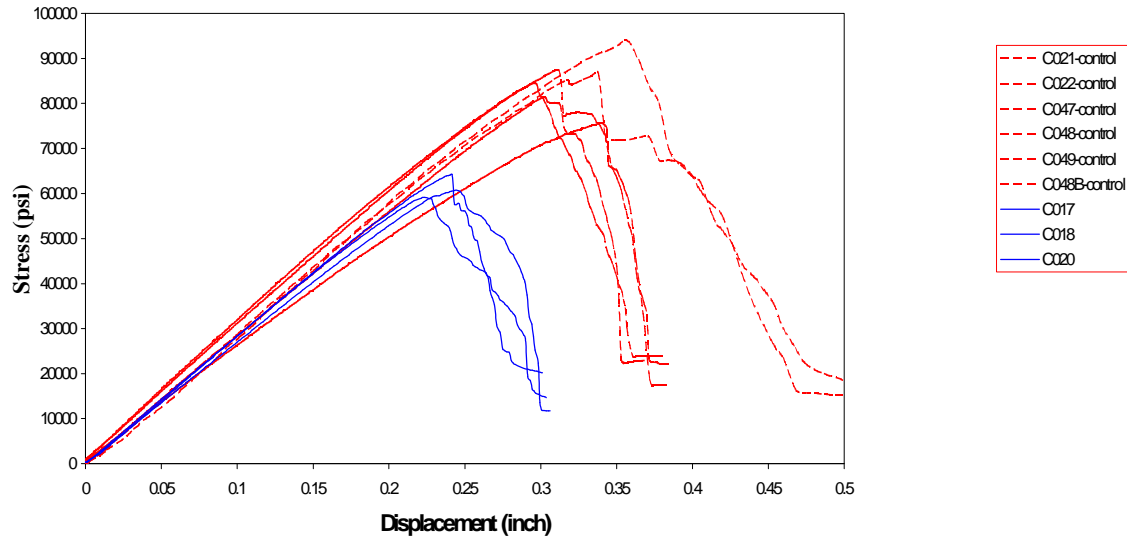
Stress vs Displacement
Iso Polyester 1
Oxygen Submersion Exposure and Controls
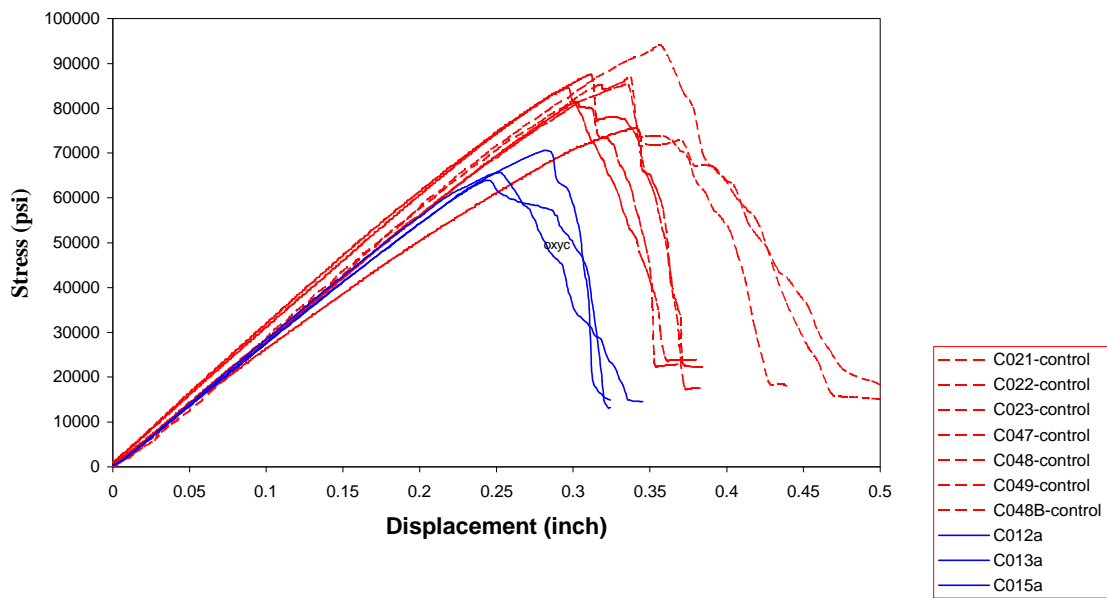
Stress vs Displacement
Iso Polyester 1
Cold Exposure and Controls
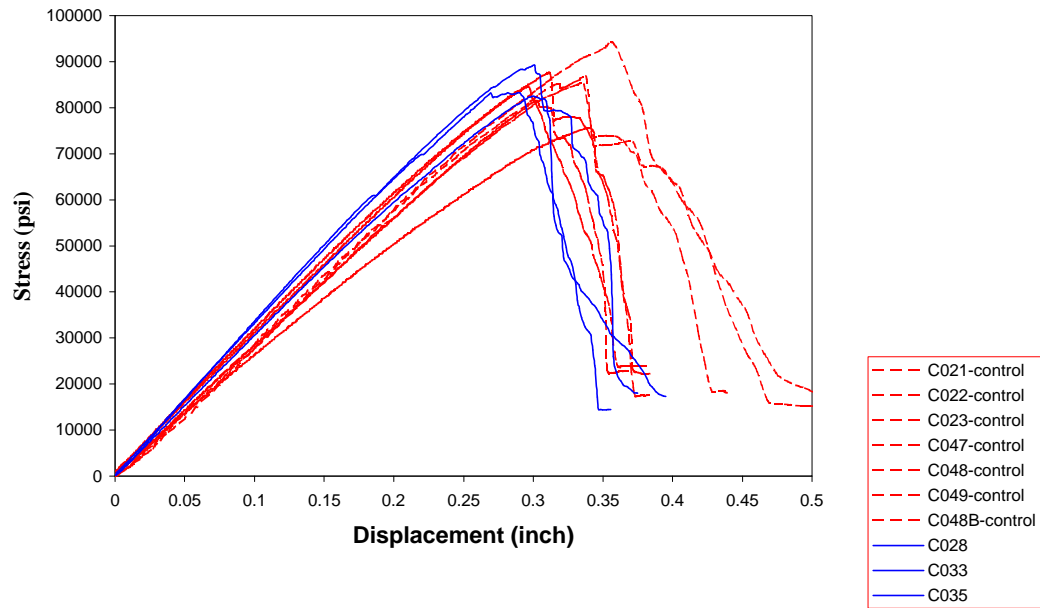
Stress vs Displacement
Iso Polyester 1
Salt Fog Exposure and Controls
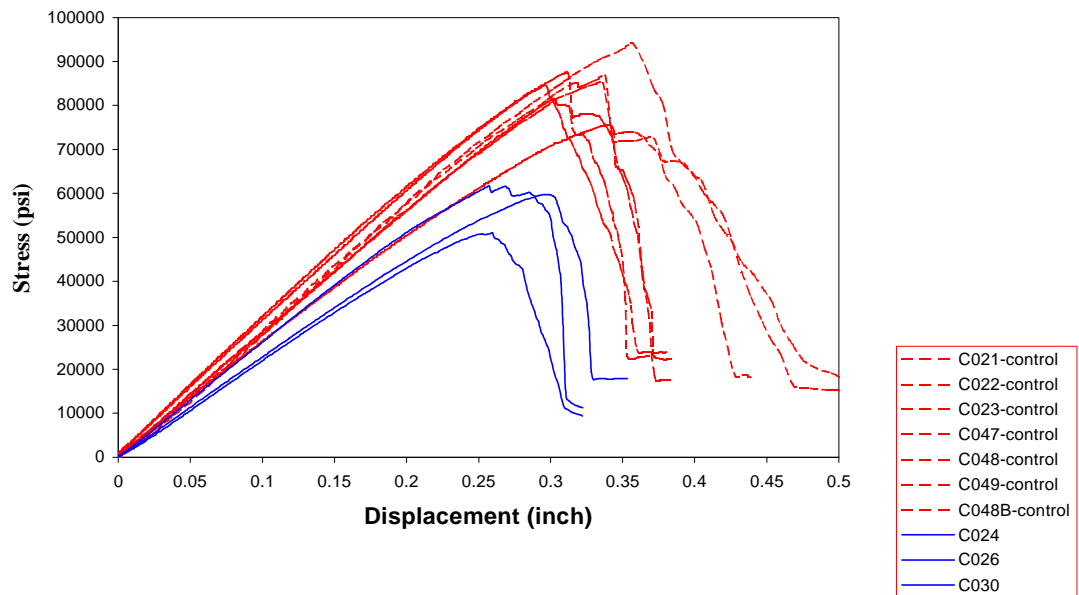
Stress vs Displacement
Iso Polyester 1
Heat Exposure and Controls

Legend:
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- C022-control
- C023-control
- C047-control
- C048-control
- C049-control
- C048B-control
- C025
- C027
- C031
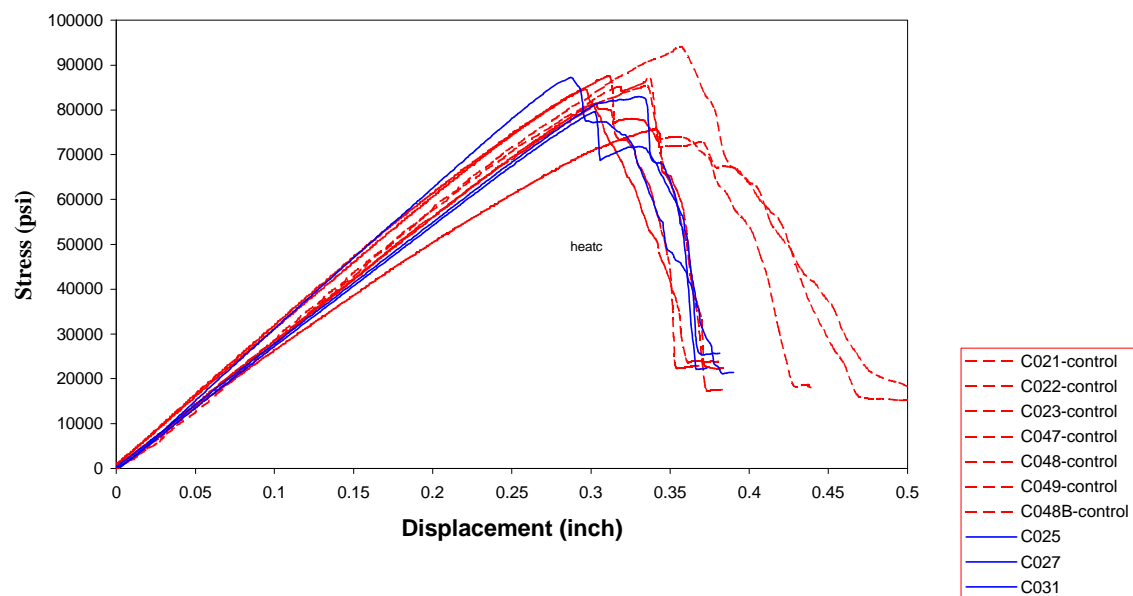
Stress vs Displacement
Iso Polyester 1
UV Exposure and Controls

Legend:
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- C022-control
- C023-control
- C047-control
- C048-control
- C049-control
- C048B-control
- C032
- C34
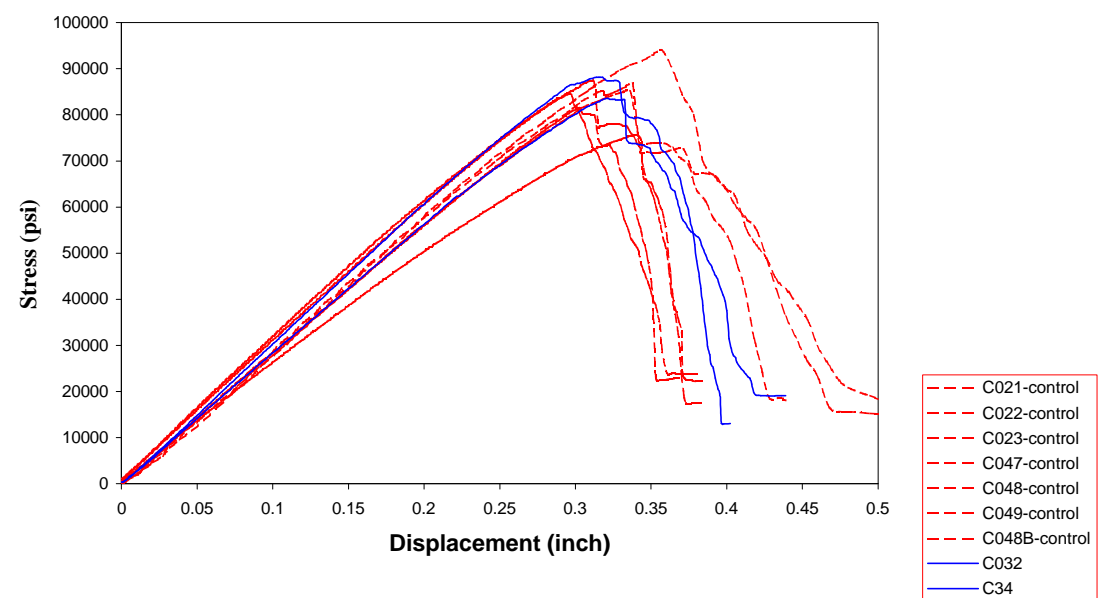
Stress vs Displacement
Iso Polyester 2
Oxygen Atmosphere Exposure and Controls
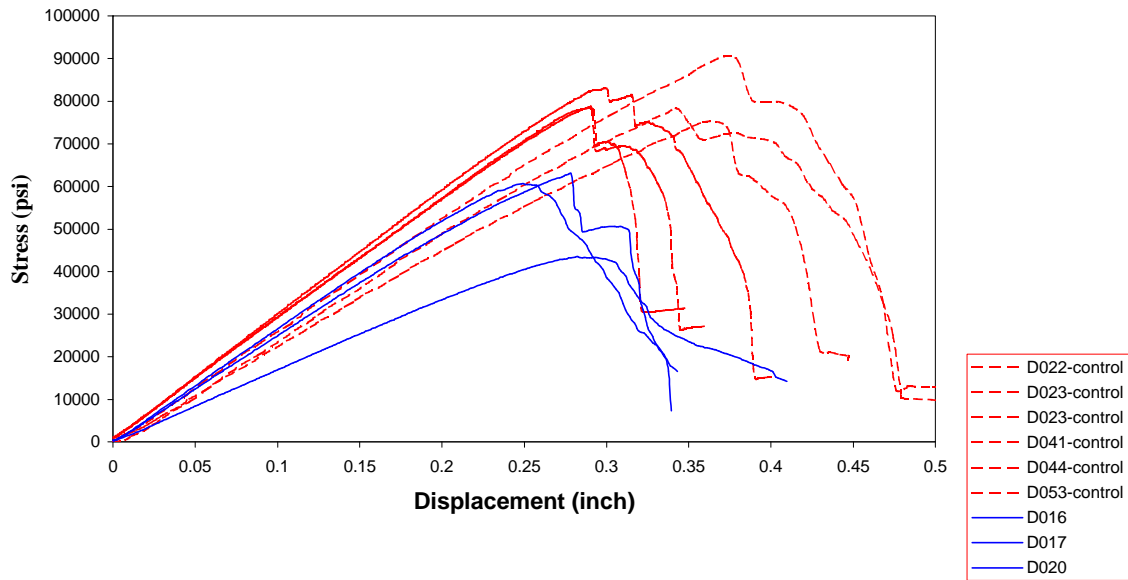
Stress vs Displacement
Iso Polyester 2
Oxygen Submersion Exposure and Controls

B - 11
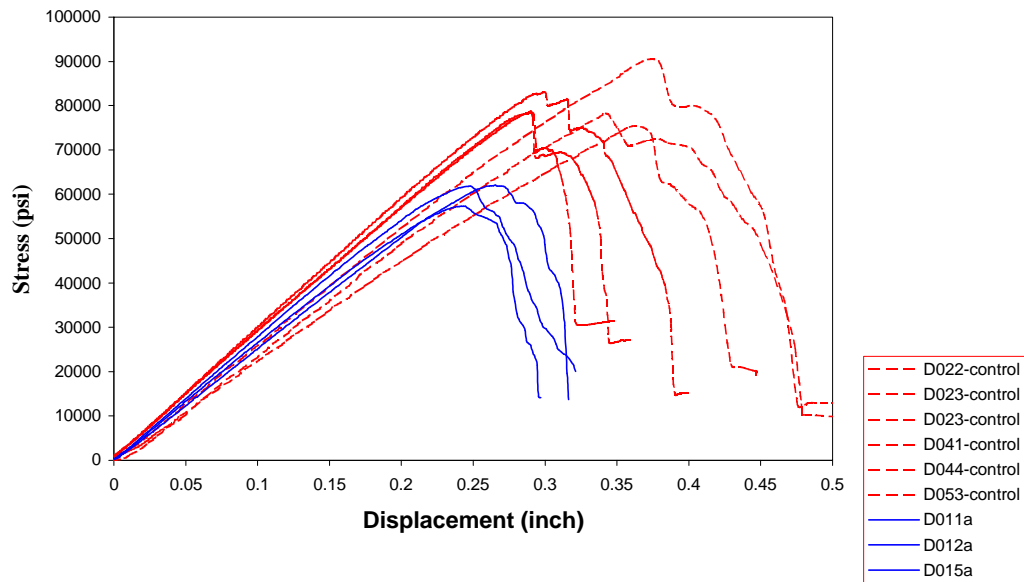
Stress vs Displacement
Iso Polyester 2
Cold Exposure and Controls
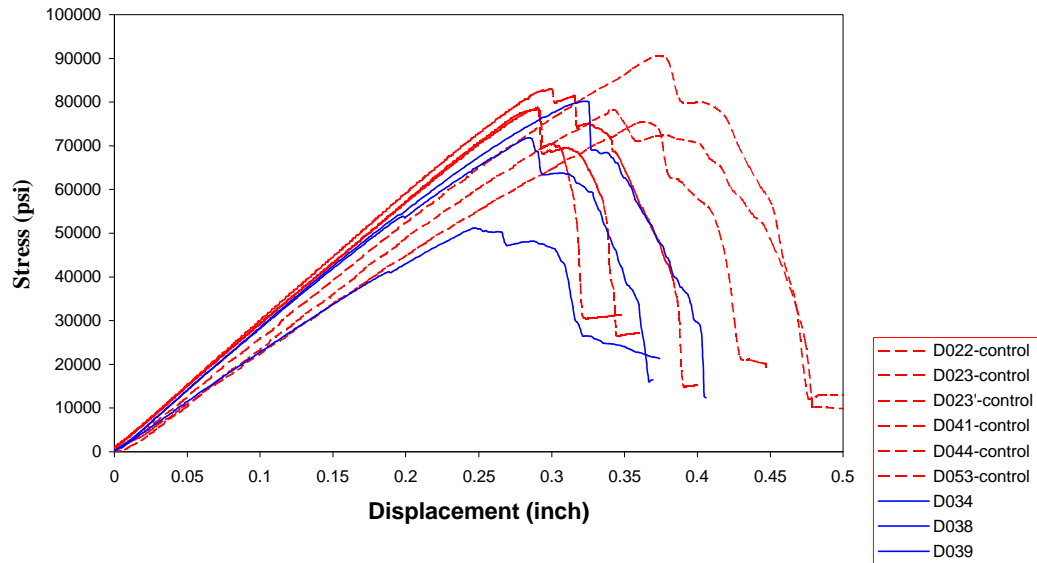
Stress vs Displacement
Iso Polyester 2
Salt Fog Exposure and Controls

B - 12
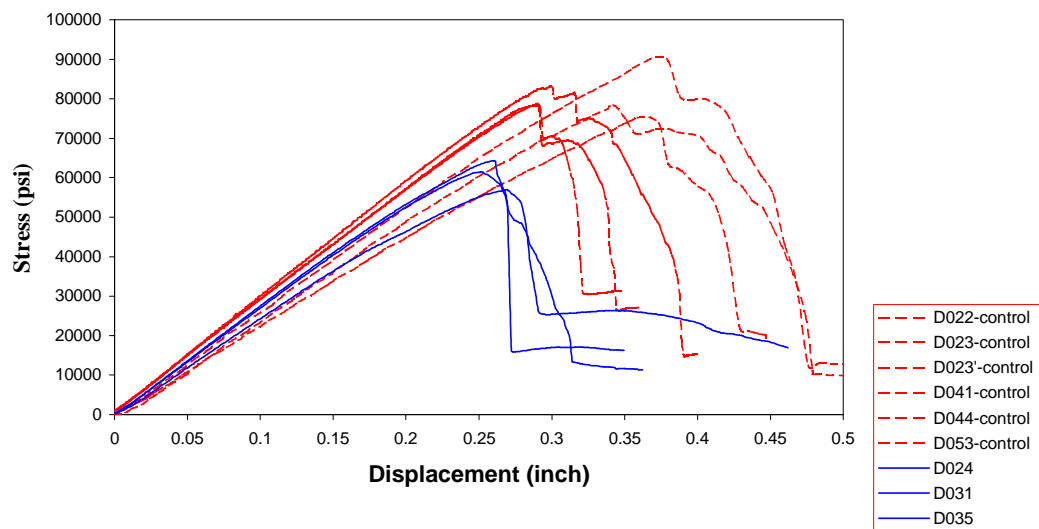
Stress vs Displacement
Iso Polyester 2
Heat Exposure and Controls

Legend:
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- D023-control
- D023-control
- D041-control
- D044-control
- D053-control
- D032
- D036
- D037
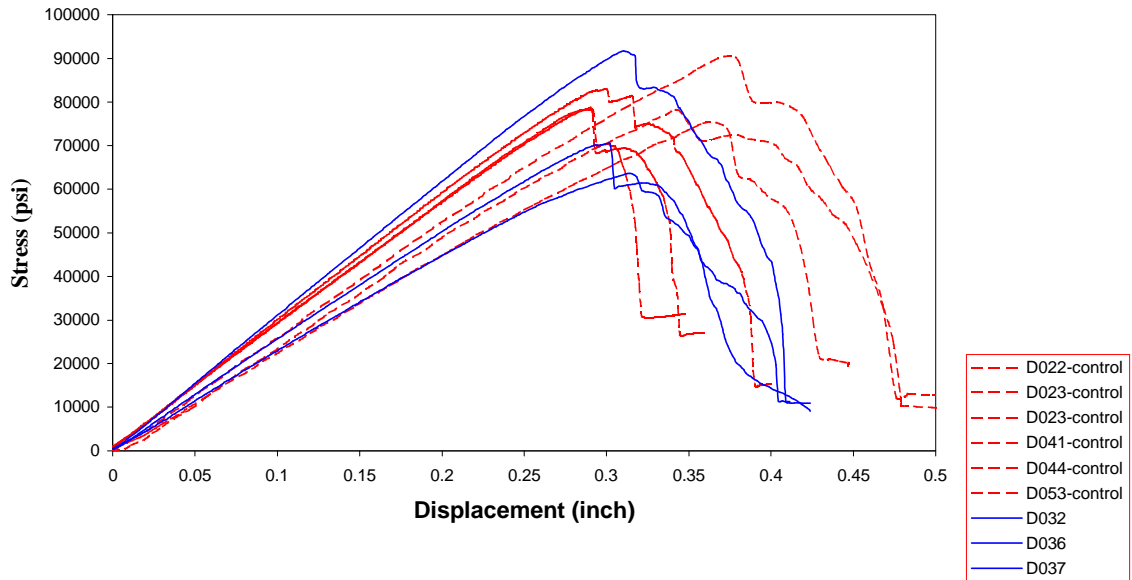
Stress vs Displacement
Iso Polyester 2
UV Exposure and Controls

Legend:
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- D023-control
- D023-control
- D041-control
- D044-control
- D053-control
- D025
- D029
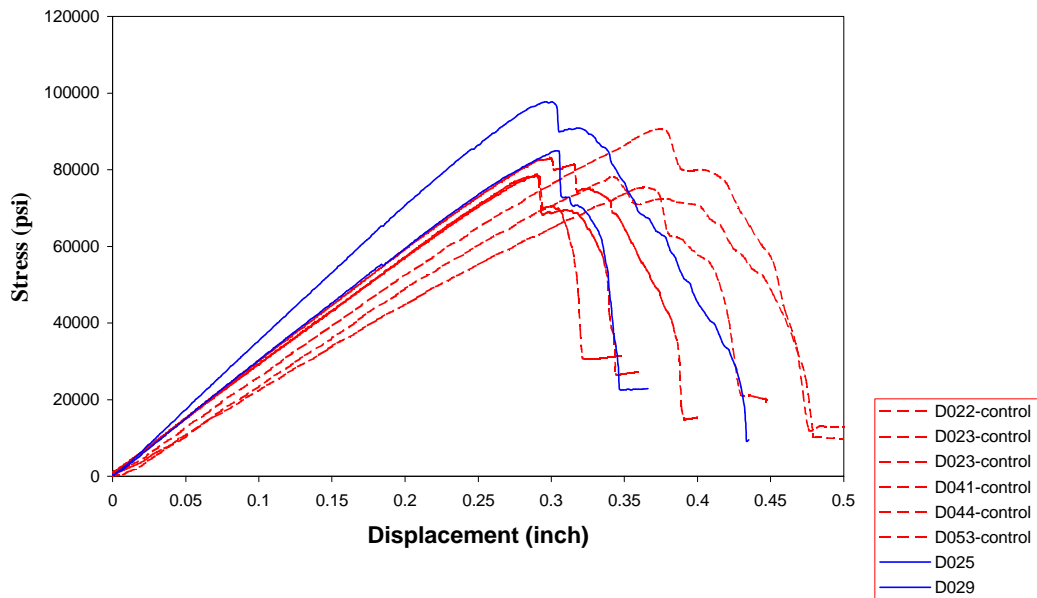
Stress vs Displacement
Phenolic-I
Oxygen Atmosphere Exposure and Controls

Legend:
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- E022-control
- E043-control
- E084-control
- E111-control
- E112-control
- E0116
- E0119
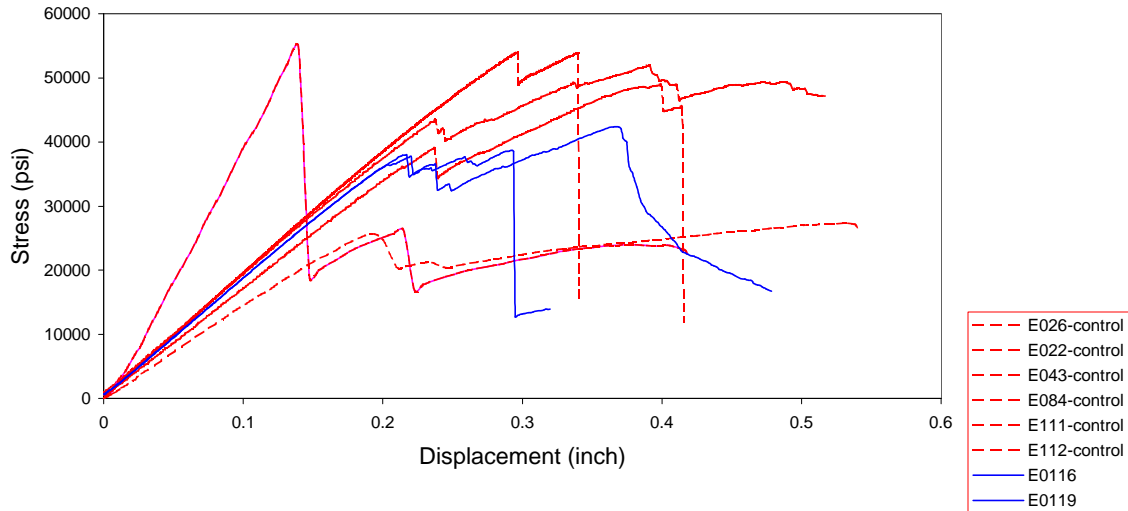
Stress vs Displacement
Phenolic-I
Oxygen Submersion Exposure and Controls

Legend:
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- E022-control
- E043-control
- E084-control
- E111-control
- E112-control
- E013a
- E014a
- E018a

B - 14
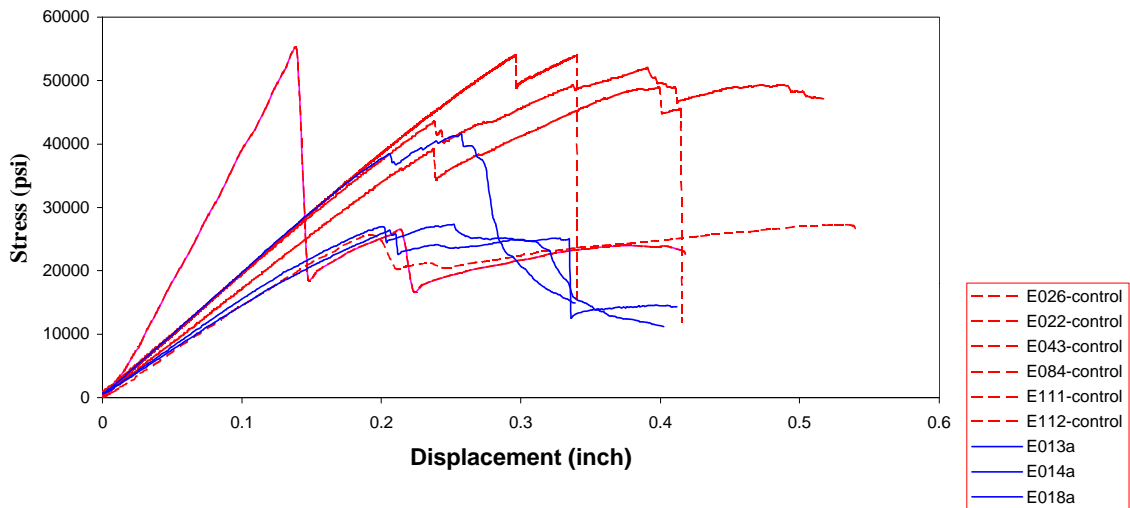
Stress vs Displacement
Phenolic I
Heat exposure and Controls

Legend:
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- E022-control
- E043-control
- E084-control
- E111-control
- E112-control
- E059
- E071
- E130
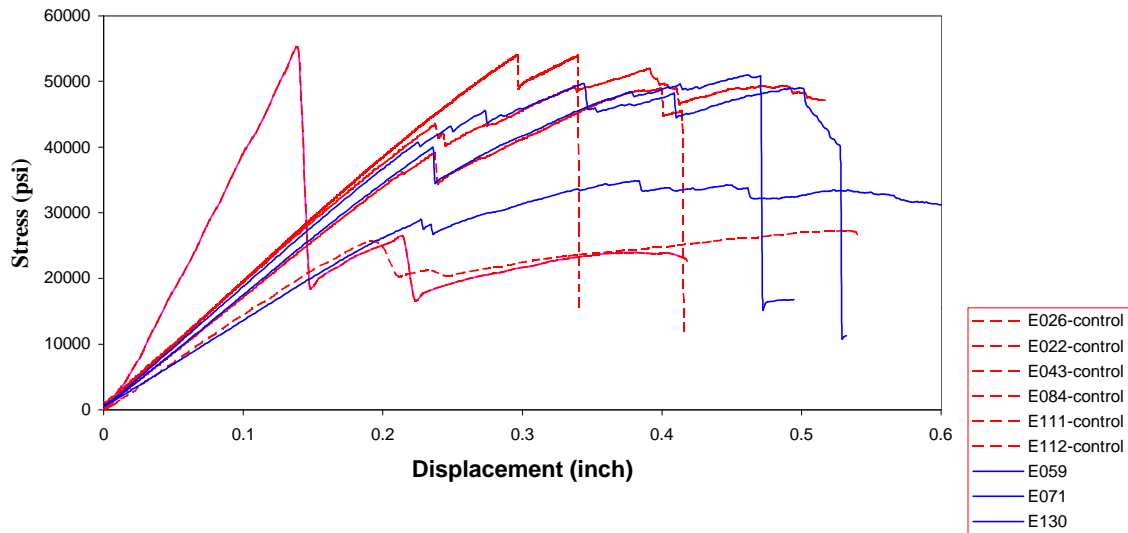
Stress vs Displacement
Phenolic 1
Salt fog Exposure and Controls

Legend:
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- E022-control
- E043-control
- E084-control
- E111-control
- E112-control
- E046
- E047
- E057
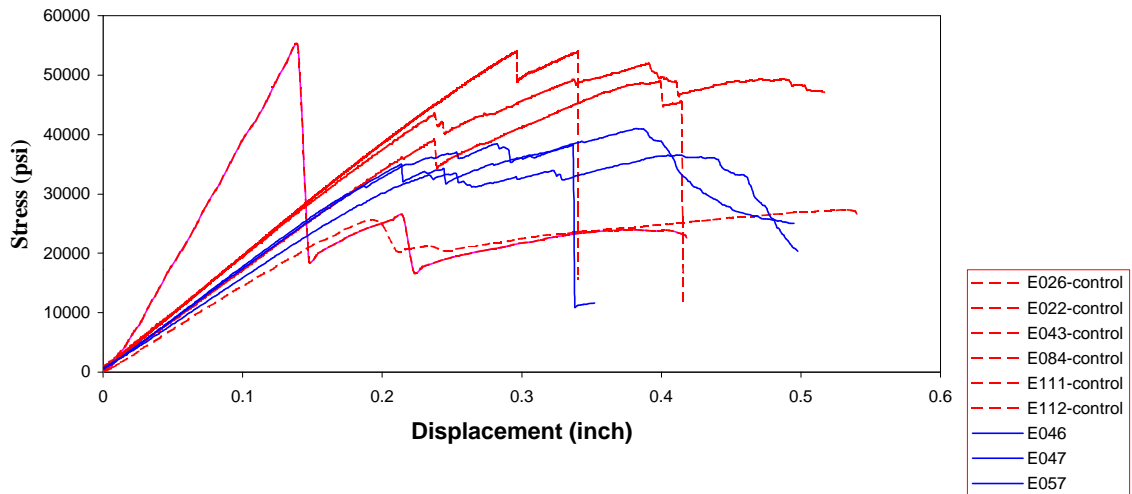
Stress vs Displacement
Phenolic 1
Cold Exposure and Controls

Legend:
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- E043-control
- E084-control
- E111-control
- E112-control
- E058
- E062
- E100
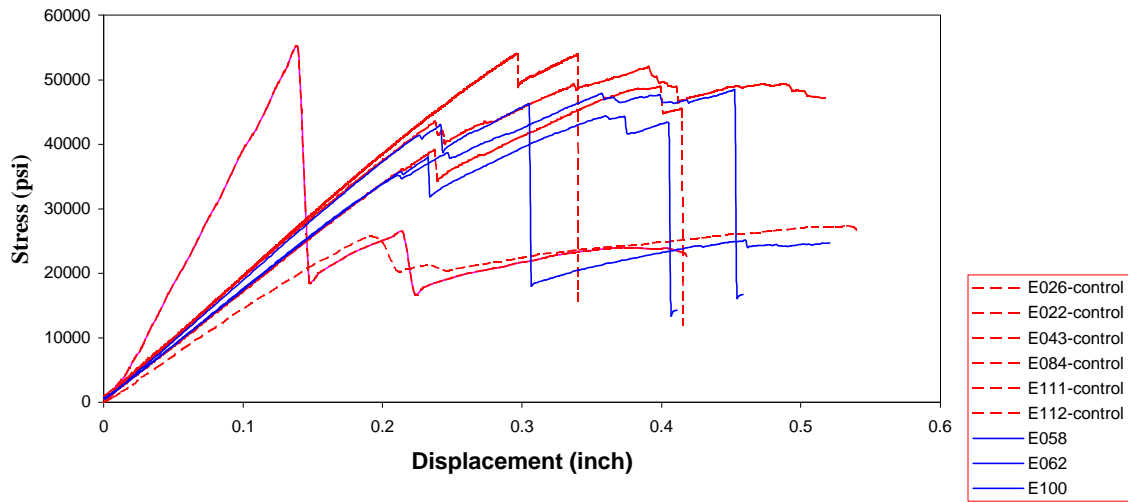
Stress vs Displacement
Phenolic-I
UV Exposure and Controls

Legend:
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- E022-control
- E043-control
- E084-control
- E111-control
- E112-control
- E053
- E085
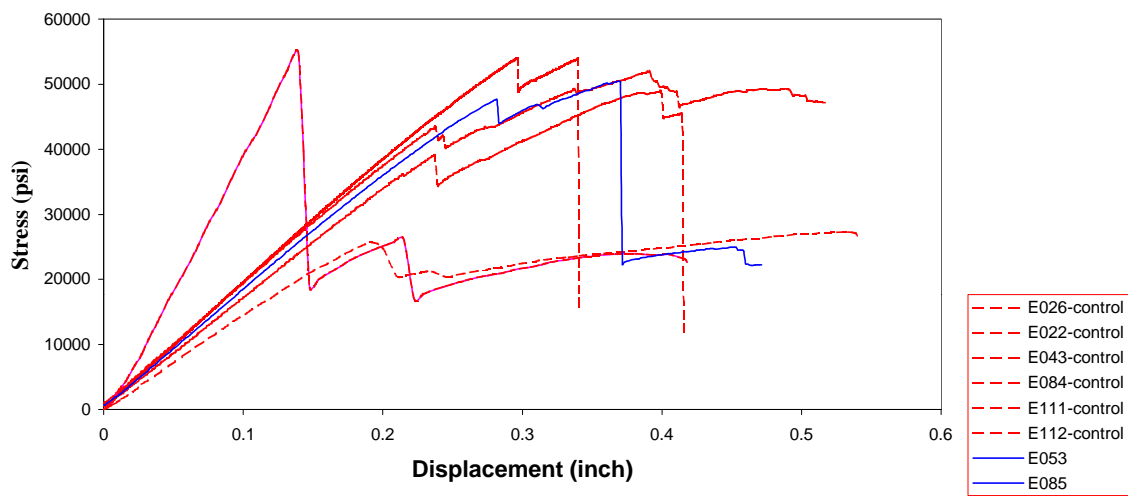
Stress vs Displacement
Phenolic-2
Oxygen Atmosphere Exposure and Controls
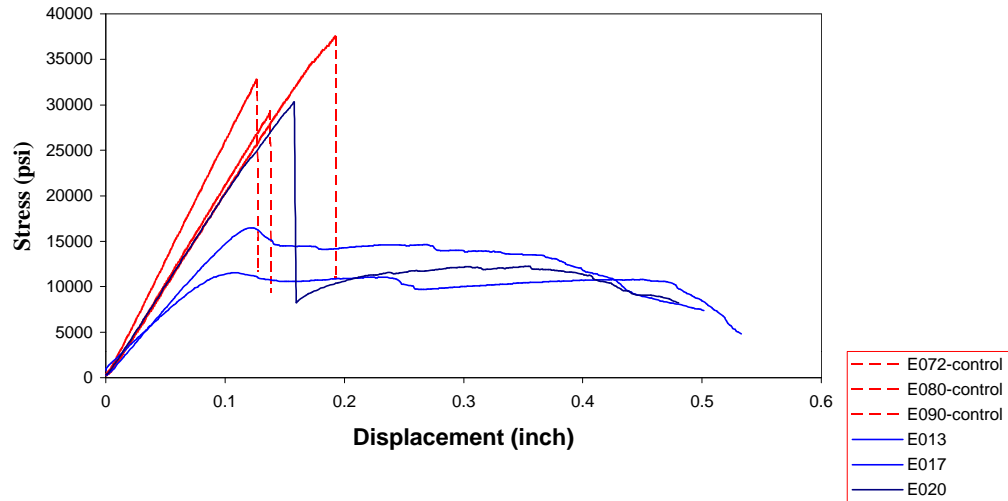
Stress vs Displacement
Phenolic-2
Oxygen Submersion Exposure and Controls

B - 17
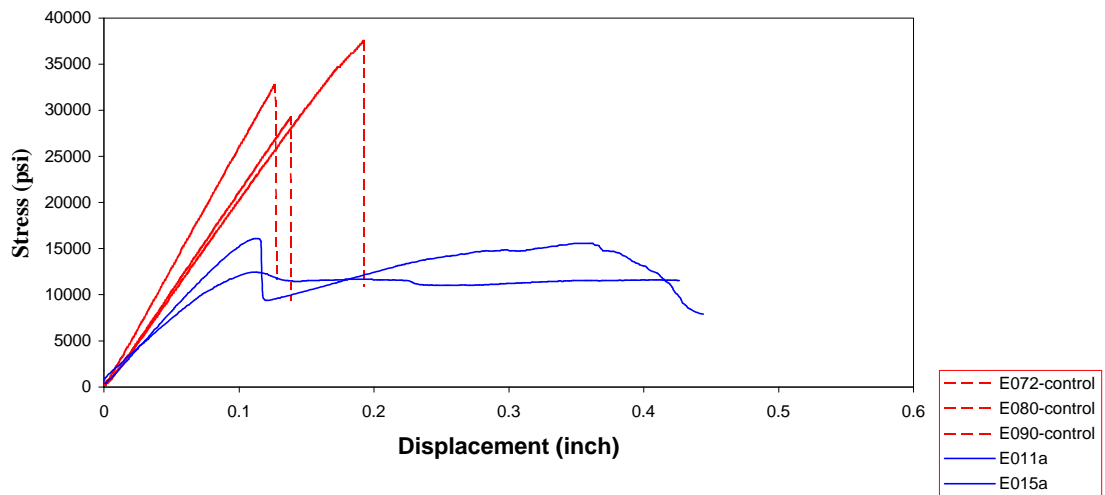
**Stress vs Displacement
Phenolic-2
Cold Exposure and Controls**
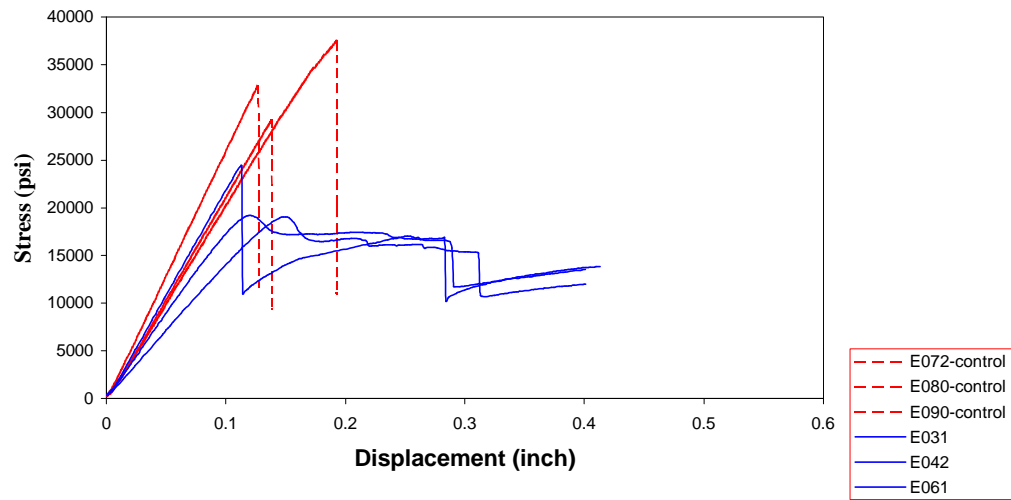
**Stress vs Displacement
Phenolic-2
Salt Fog Exposure and Controls**
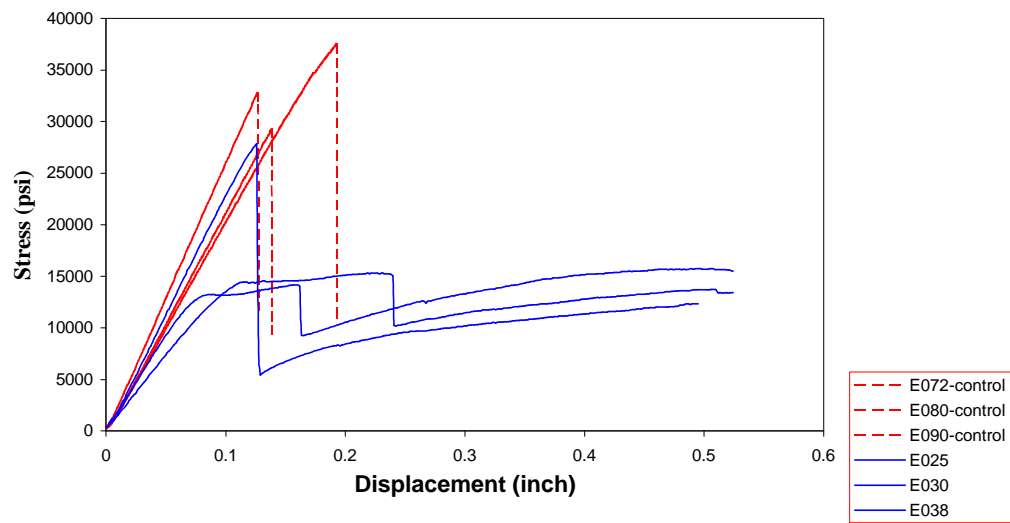
**Stress vs Displacement
Phenolic-2
Heat Exposure and Controls**

Legend:
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- E080-control (red dashed)
- E090-control (red dashed)
- E024 (blue)
- E039 (blue)
- E040 (blue)
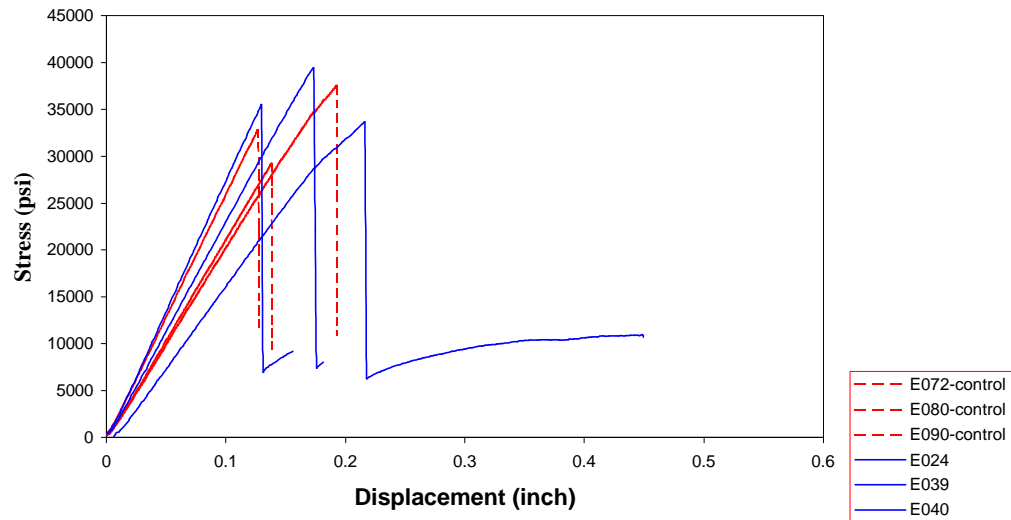
**Stress vs Displacement
Phenolic-2
UV Exposure and Controls**

Legend:
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- E080-control (red dashed)
- E090-control (red dashed)
- E032 (blue)
- E051 (blue)
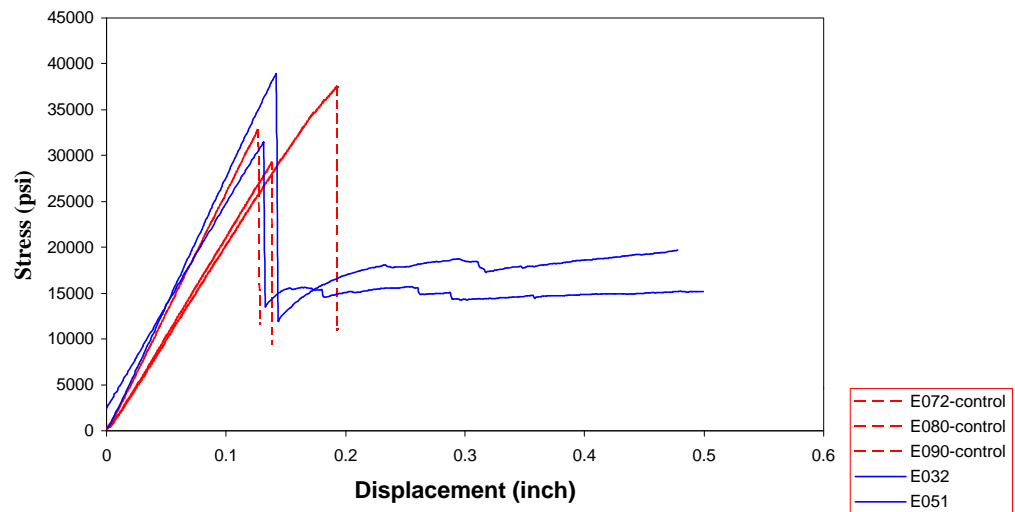
Stress vs Displacement
Epoxy
Oxygen Atmosphere Exposure and Controls
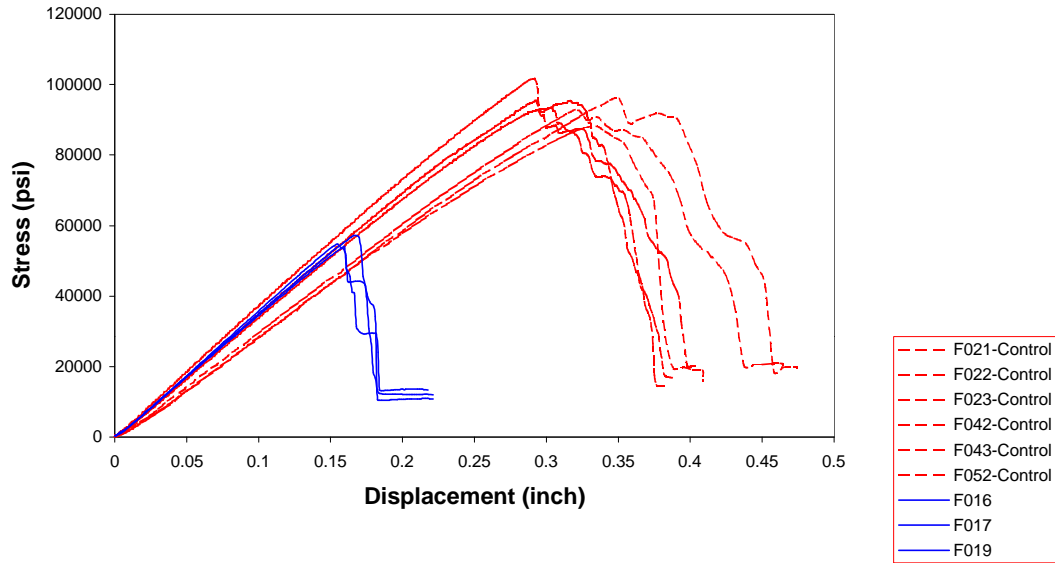
Stress vs Displacement
Epoxy
Oxygen Submersion Exposure and Controls
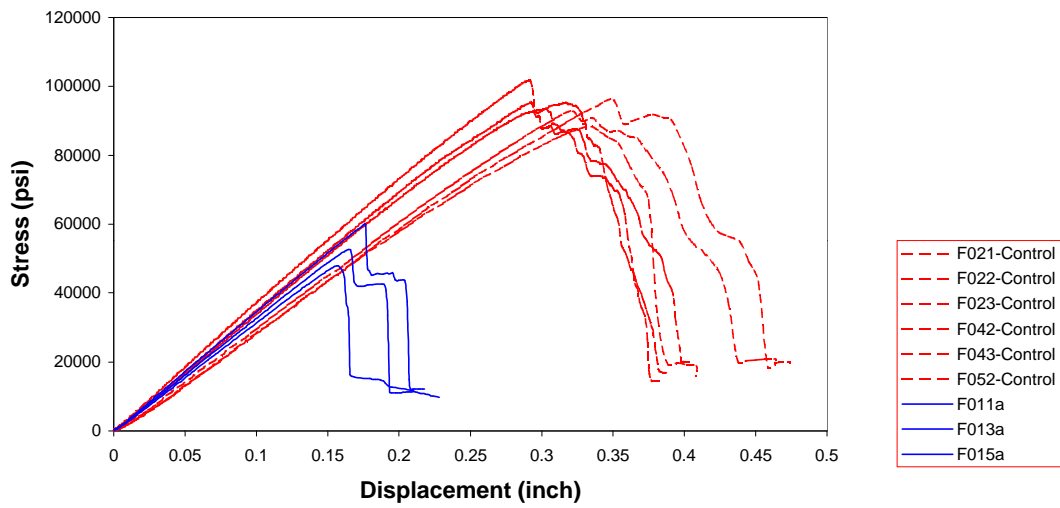
Stress vs Displacement
Epoxy
Cold Exposure and Controls
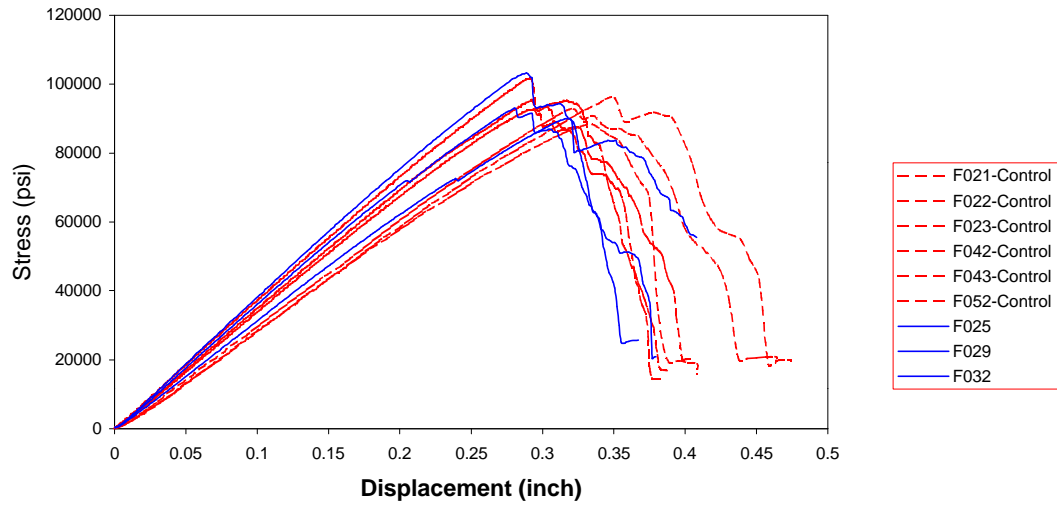
Stress vs Displacement
Epoxy
Salt Fog Exposure and Controls
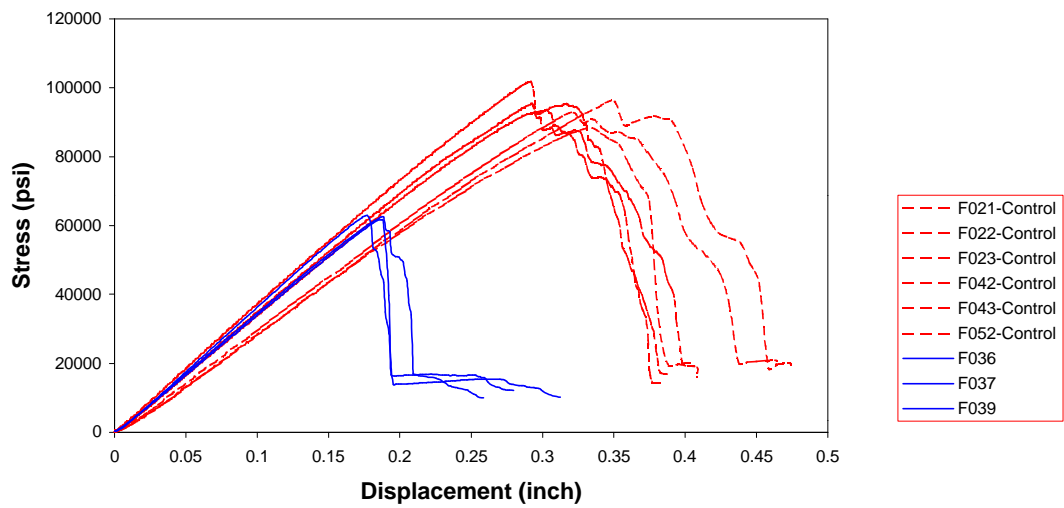
Stress vs Displacement
Epoxy
Heat Exposure and Controls
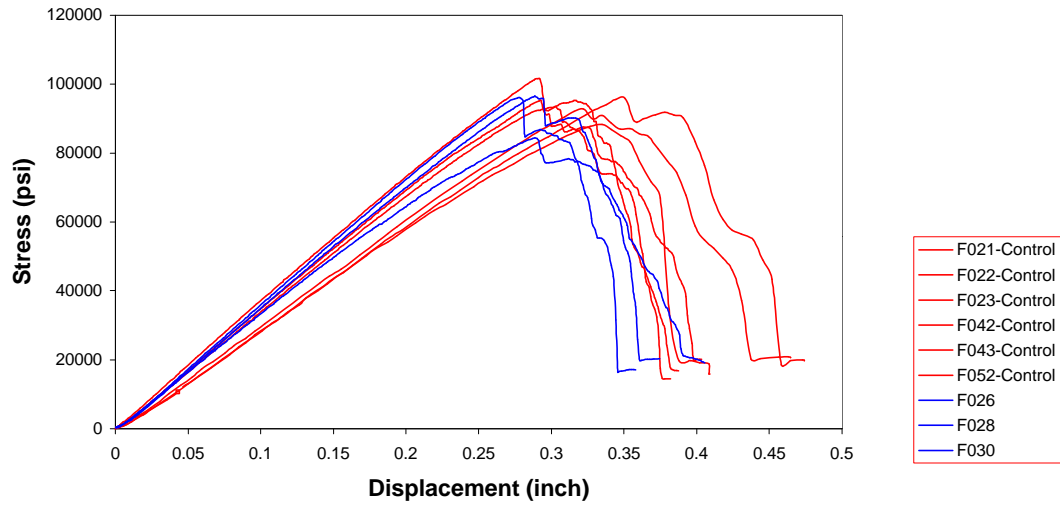
Stress vs Displacement
Epoxy
UV Exposure and Controls
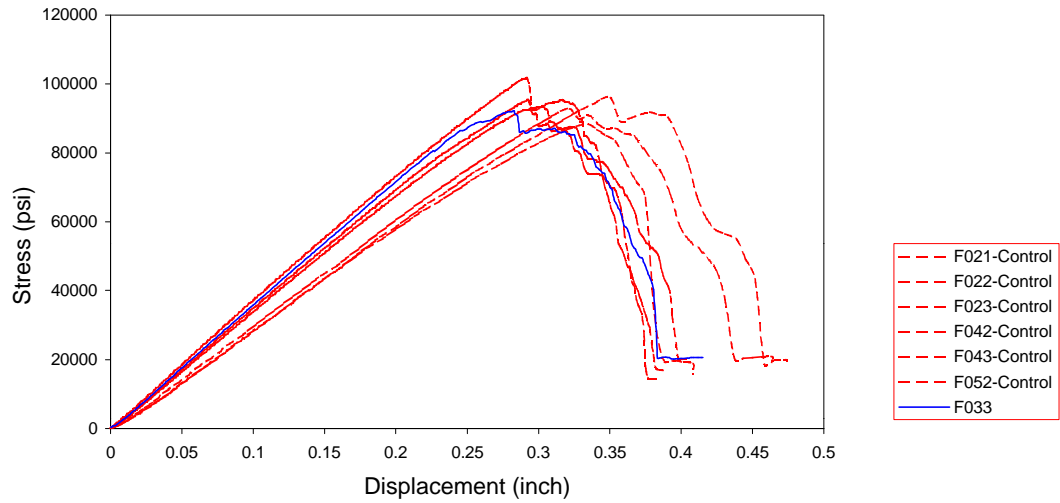
APPENDIX C – SUMMARY OF TENSILE STRENGTH DATA

This appendix includes the tensile strength data for both controls and weathered specimens. In the following graphs, the nomenclature is as follows:

(1) Control specimen – CONTROL
(2) Oxygen (100%) and salt water spray (100ºF) for 12 months – OXYGEN ATM
(3) Oxygen (100%) and salt water immersion (100ºF) for 12 months – OXYGEN SUB
(4) Cold freezer (-4ºF) – not completed
(5) Salt fog tank (95ºF) at 28 days and 18 months – SALT FOG
(6) Dry heat oven (95ºF) – not completed
(7) Ultraviolet exposure unit (70ºC or 158ºF cycles) – not completed

FRP Tensile Strength
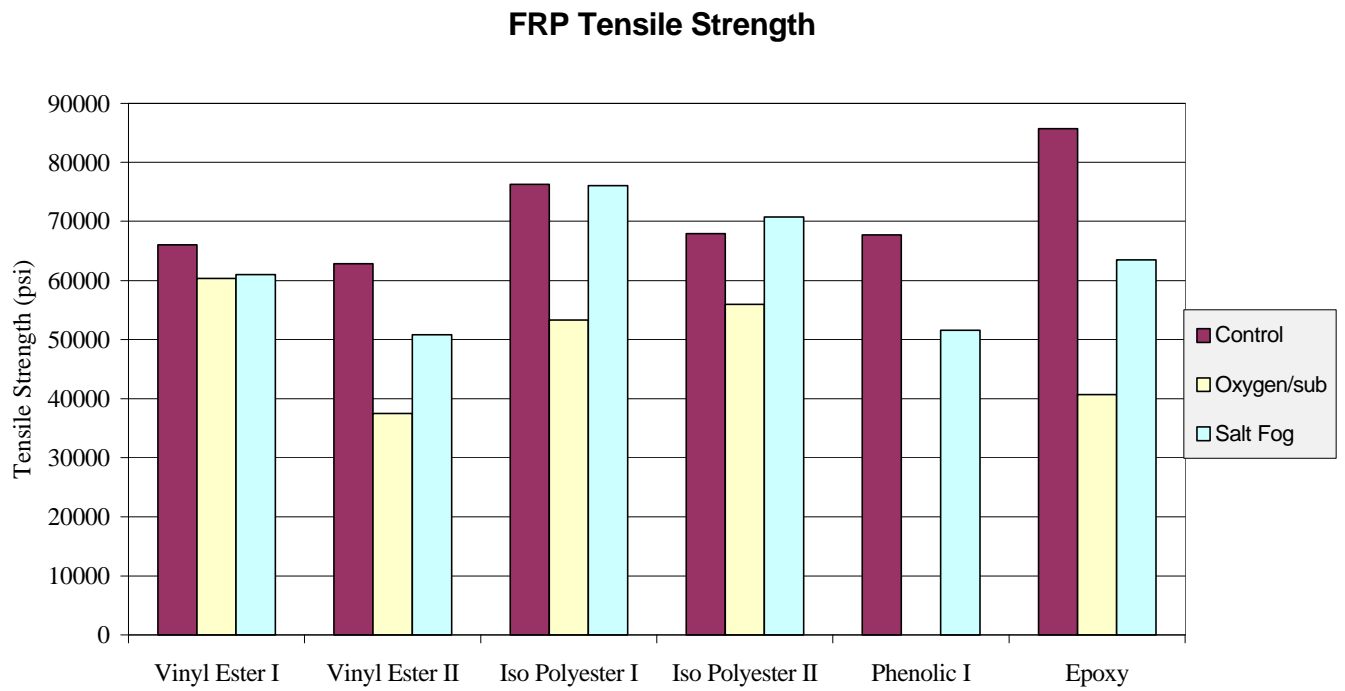
FIGURE C-1. TENSILE STRENGTH OF CONTROL AND EXPOSED FRP SPECIMENS

TABLE C-1. SUMMARY OF TENSILE TESTING DATA

FRP Tensile Test Data					
Material	**Tensile Strength (PSI)**			28 day	18 month
	Control	Oxygen/atm	Oxygen/sub	Salt Fog	Salt Fog
A Vinyl Ester I	70591	60333	63471	62202	66351
B Vinyl Ester II	60146	37527	42380	56662	55367
C Iso Polyester I	76279	53347	55942	75854	61554
D Iso Polyester II	68849	55965	46687	65658	60847
E Phenolic I	67731	-	-	51619	48867
F Epoxy	85694	40684	39392	63481	52556
Material	**Modulus of Elasticity (PSI)**			28 day	18 month
	Control	Oxygen/atm	Oxygen/sub	Salt Fog	Salt Fog
A Vinyl Ester I	3.63E+06	4.18E+06	4.14E+06	3.87E+06	4.07E+06
B Vinyl Ester II	3.90E+06	3.82E+06	3.83E+06	3.57E+06	4.06E+06
C Iso Polyester I	3.71E+06	3.24E+06	3.83E+06	3.83E+06	4.03E+06
D Iso Polyester II	3.73E+06	3.83E+06	3.49E+06	3.39E+06	3.76E+06
E Phenolic I	4.26E+06	-	-	3.96E+06	3.17E+06
F Epoxy	4.63E+06	4.36E+06	4.57E+06	4.19E+06	4.33E+06

APPENDIX D – DMA PARAMETERS AND ANALYSES

All samples were manufactured in June 1996 by Strongwell, Inc. (formerly MMFG. Co.). Conditioning prior to the DMA tests consisted of storing the samples in open air in a temperature-controlled room. Temperature and humidity were kept at approximately 22ºC (72ºF) and 50% RH (relative humidity), respectively. The original dimensions of each composite piece were 10" x 0.5" x 0.125". All sample strips were stamped and weighed prior to analysis and exposure.

Instrument Information: DMA-983   (TA Instruments)

- Fixed frequency mode at 1 Hz.
- Vertical serrated clamps
- 14.5 in-lb clamp torque for esters and epoxy, 12 in-lb for phenolic

The calibration of the DMA instrument for the following parameters was performed in accordance with the manufacturer's instructions:

- Moment of Inertia - calibrated when instrument is installed or moved.
- Parallel Storage Stiffness - calibrated 1x/month.
- Parallel Loss Stiffness - calibrated 1x/month.
- Drive Signal Constant - calibrated 1x/month.
- Series Storage Compliance - calibrated 1x/month.
- Series Loss Compliance - calibrated 1x/month.
- Phase Angle - calibrated 1x/week

All calibration parameters were within specification values.

Length correction was performed on each material type for both control and exposed samples.

Control Samples – Analysis Notes:

Vinylester I: There is approximately a 5% difference from sample to sample in the room-temperature modulus values. The T_g values are fairly consistent but the peaks are somewhat broad, suggesting undercure of the resin. Length correction (a necessary calibration for stiff samples that compensates for movement of the sample in the clamped ends) was performed several times, but the values were inconsistent with fairly large standard deviations.

Vinylester II: Relatively close modulus values with consistent T_g values (although some variation in peak height). Length corrections were inconsistent with a similar range of values as for the Vinylester I.

Isopolyester I: This material has the closest modulus values from sample to sample, although the E" peaks are fairly broad. Very good length correction (small standard deviation). Consistent T_g values.

Isopolyester II: This material has a fairly wide range of modulus values from sample to sample. Broad E" peaks. Samples appear to be heterogeneous and undercured.

Phenolic II: Samples are <u>uncharacteristically</u> soft (phenolics are thermosets and should be hard). Wide range of modulus values. Very broad E".   Samples were harder to set into the clamps (i.e. softer - clamps embedded into the sample). Performed two length corrections and obtained fairly consistent values.

Epoxy: Fairly wide range of modulus. Relatively consistent T_g, values although some variations in peak height. These samples gave the highest modulus values of all the composite types.

TABLE D-1. DMA TESTING DETAILS

Name and Codes of Specimens	Typical Dimensions	Average Amplitudes	Temperature Program
Vinylester I A008.1, A005.2, A006.2, , A029, A035, A038, A024, A025, A033	6 x 3.2 mm 49.9 mm clamped length	0.7 - 1.0 mm	50 -155 C. at 2 deg/min
Vinylester II B007.1, B008.1, B010.1, B034, B036, B038, B032, B037, B047	6 x 3.2 mm 49.9 mm clamped length	0.8 –1.0 mm	50 -155 C. at 2 deg/min
Isopolyester I C006.2, C007.1, C009.1, C024, C026, C030, C028, C033, C035	6 x 3.2 mm 49.9 mm clamped length	0.8 - 1.0 mm	40-135 C. at 2 deg/min
Isopolyester II D006.1, D009.1, D010.1, D024, D031, D035, D034, D038, D039	6 x 3.2 mm 49.9 mm clamped length	0.7 - 1.0 mm	40-135 C. at 2 deg/min
Phenolic II E008.1, E009.1, E010.1, , E025, D042, E061, E031, E042,	6 x 3.3 mm 40 mm clamped length	0.9 - 1.1 mm	40-210 C. at 2 deg/min
Epoxy F009.1, F010.1, F006.2, F036, F039, F037, F025, F028, F038	6 x 3.3 mm 49.9 mm clamped length	0.6 - 0.8 mm	50-185 C. at 2 deg/min

**Starting Flexural Storage Modulus E' (Gpa)
with Standard Deviation Margins**
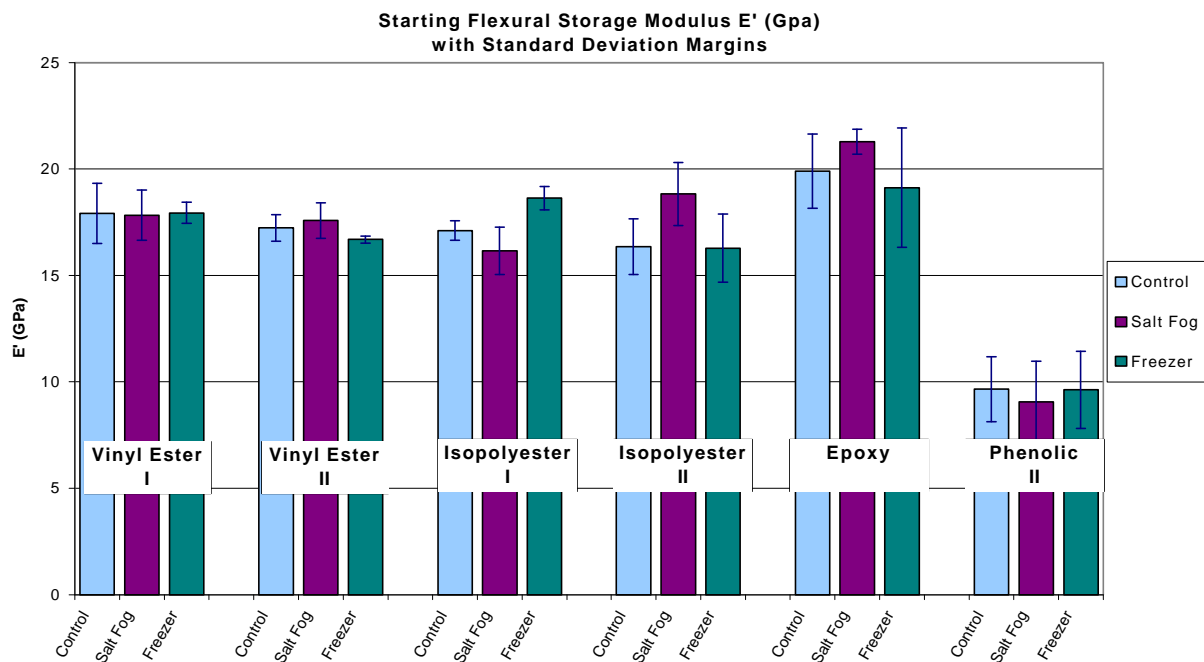
FIGURE D-1   DMA DATA FOR STARTING FLEXURAL MODULUS.

**Glass Transition Temperature - Tg (degrees Celsius)
with Standard Deviation Margins**
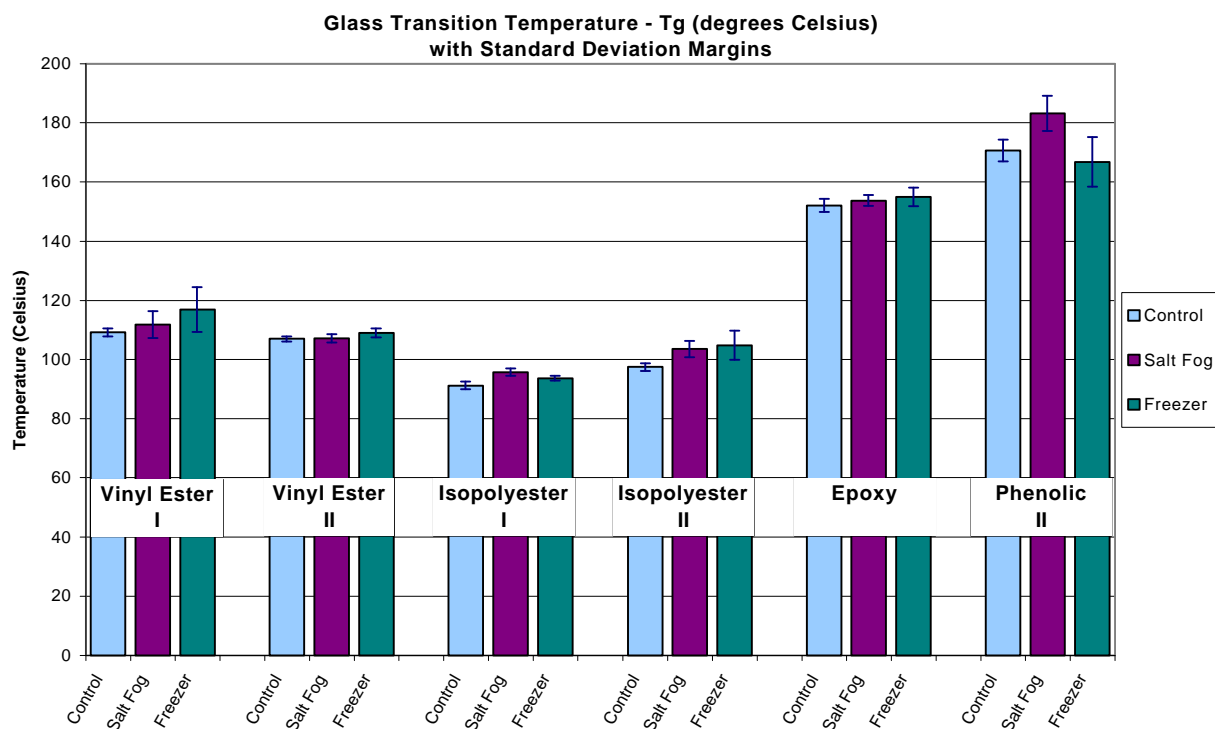
FIGURE D-2   DMA DATA FOR GLASS TRANSITION MEASUREMENTS.
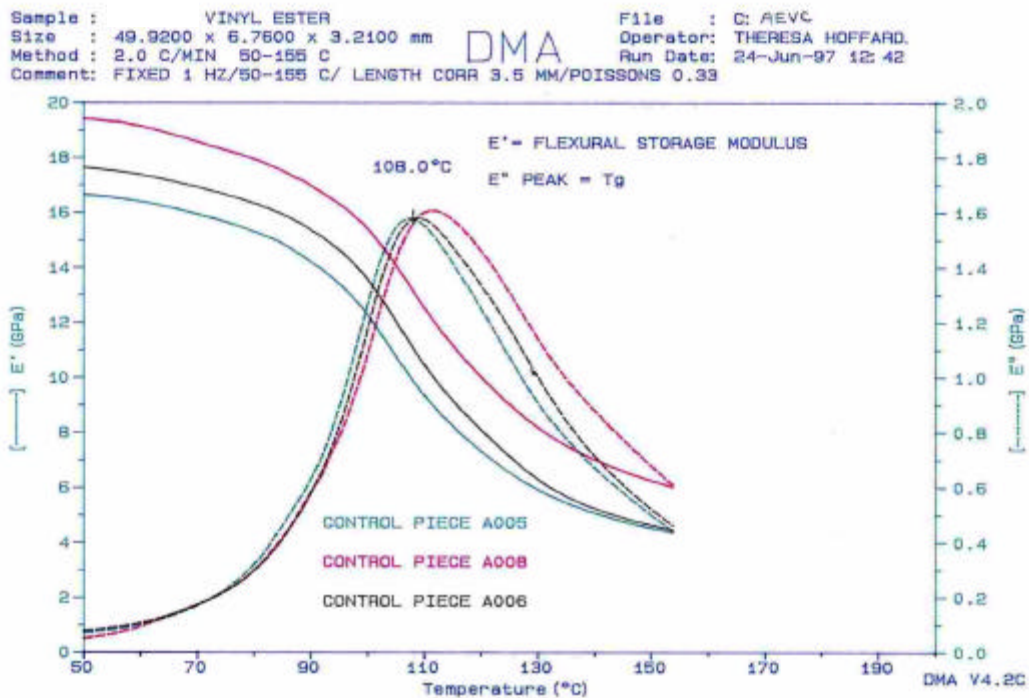
FIGURE D-3. DMA CONTROL RESULTS FOR VINYLESTER I.
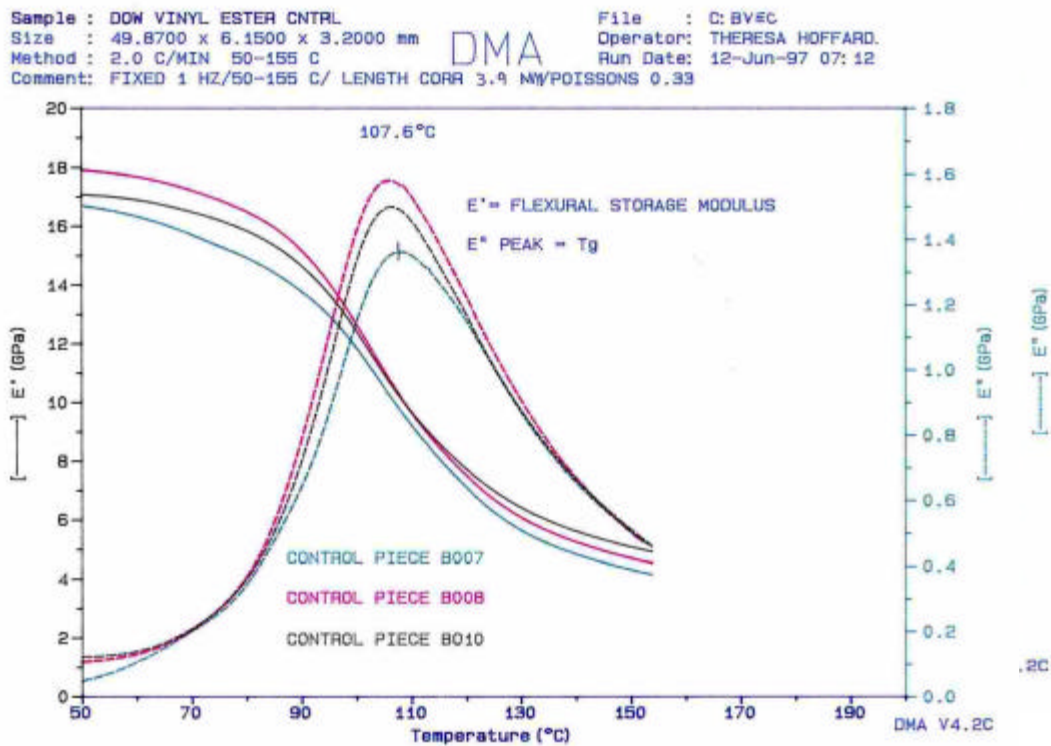
FIGURE D-4. DMA CONTROL RESULTS FOR VINYLESTER II.

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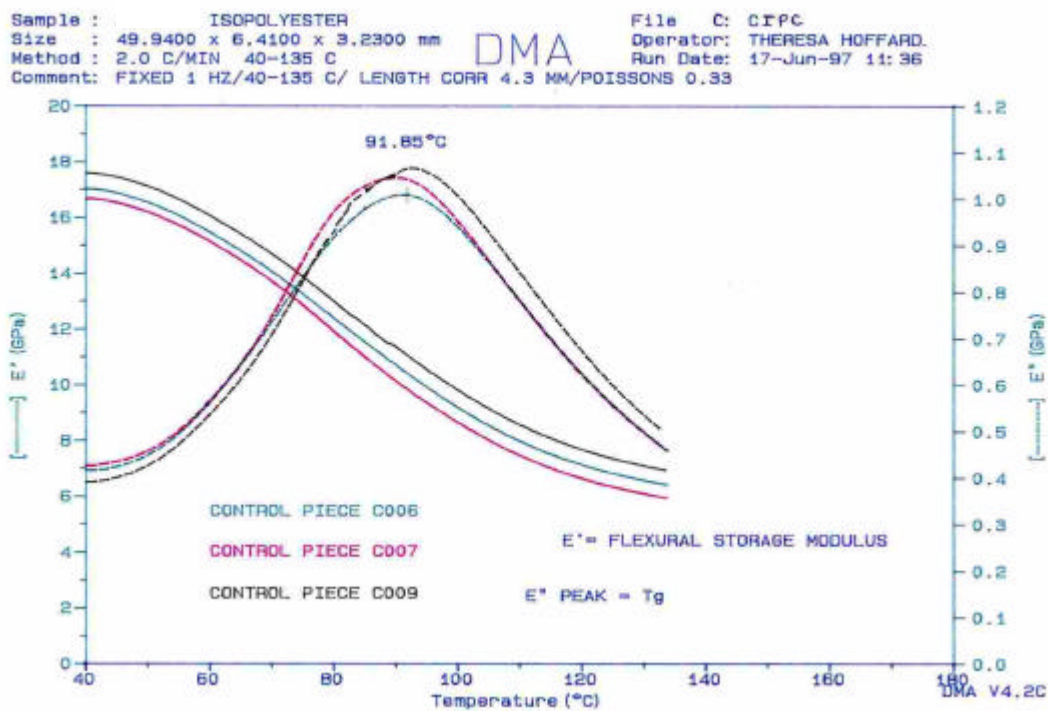
FIGURE D-5. DMA CONTROL RESULTS FOR POLYESTER I.
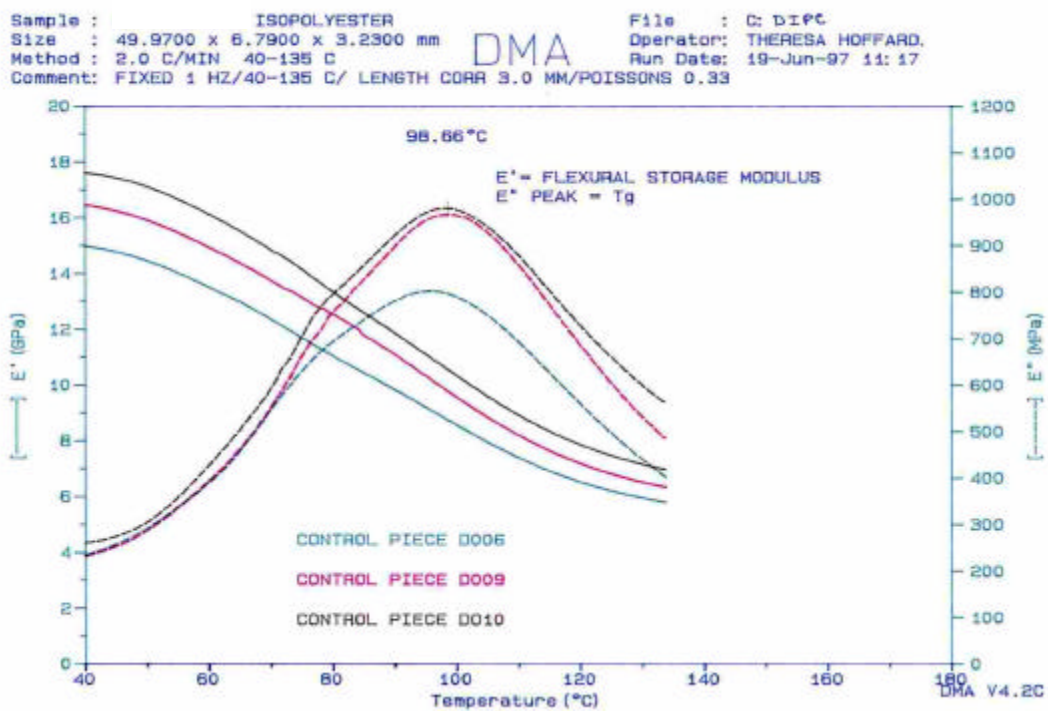
FIGURE D-6. DMA CONTROL RESULTS FOR POLYESTER II.
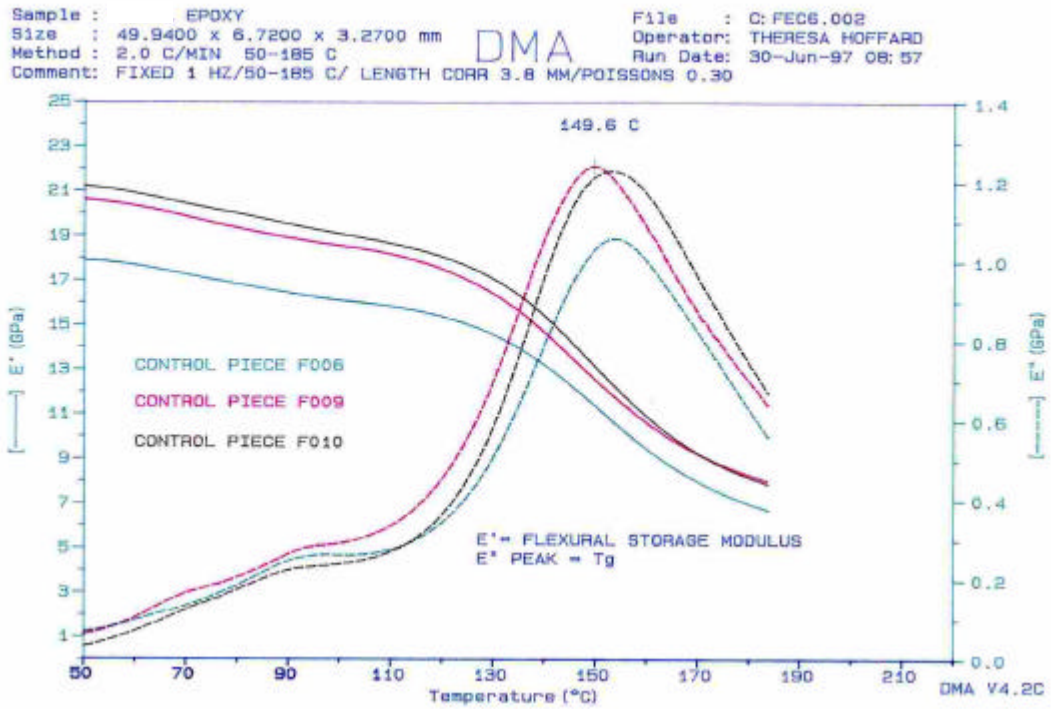
FIGURE D-7. DMA CONTROL RESULTS FOR EPOXY.
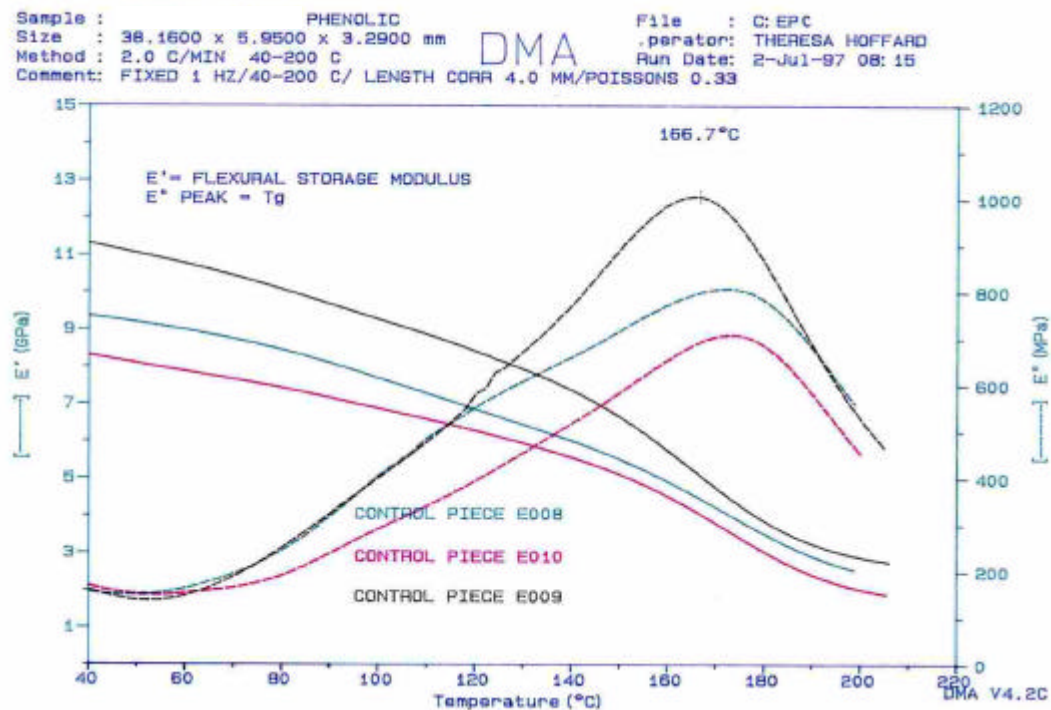
FIGURE D-8. DMA CONTROL RESULTS FOR PHENOLIC II.
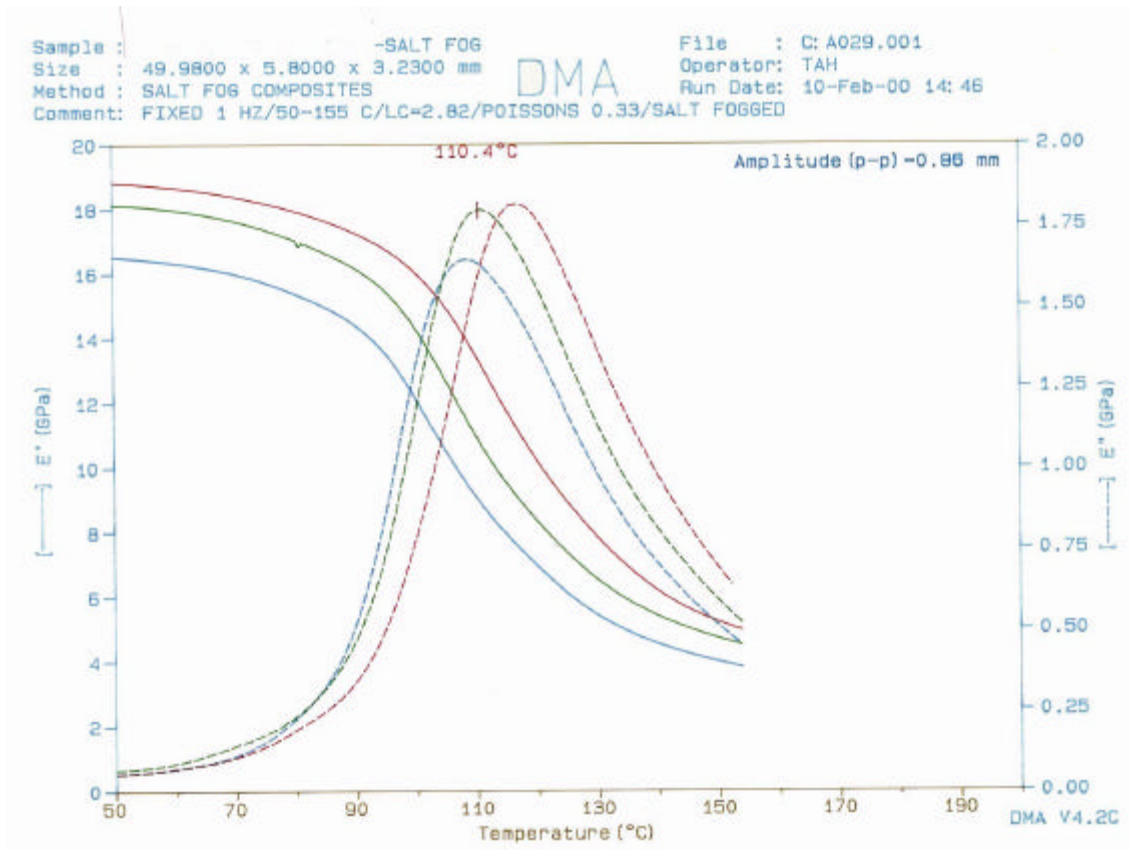
FIGURE D-9. DMA SALT FOG RESULTS FOR VINYLESTER I.
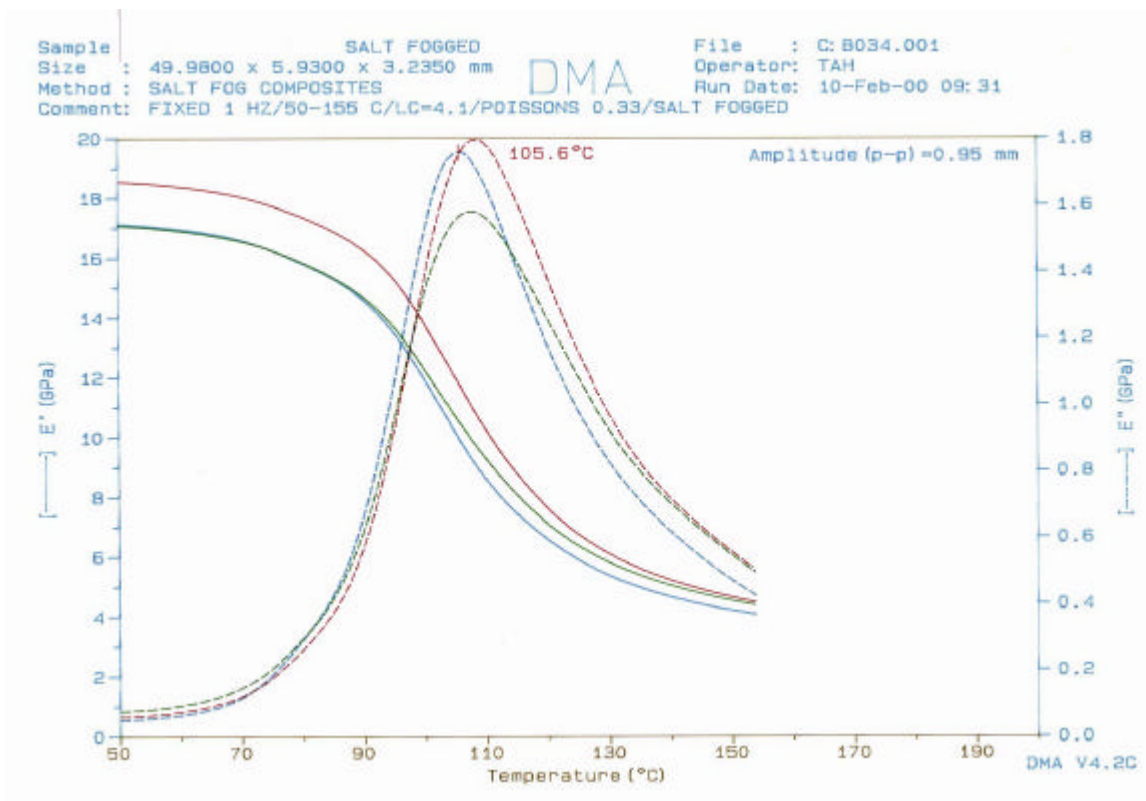
FIGURE D-10. DMA SALT FOG RESULTS FOR VINYLESTER II.
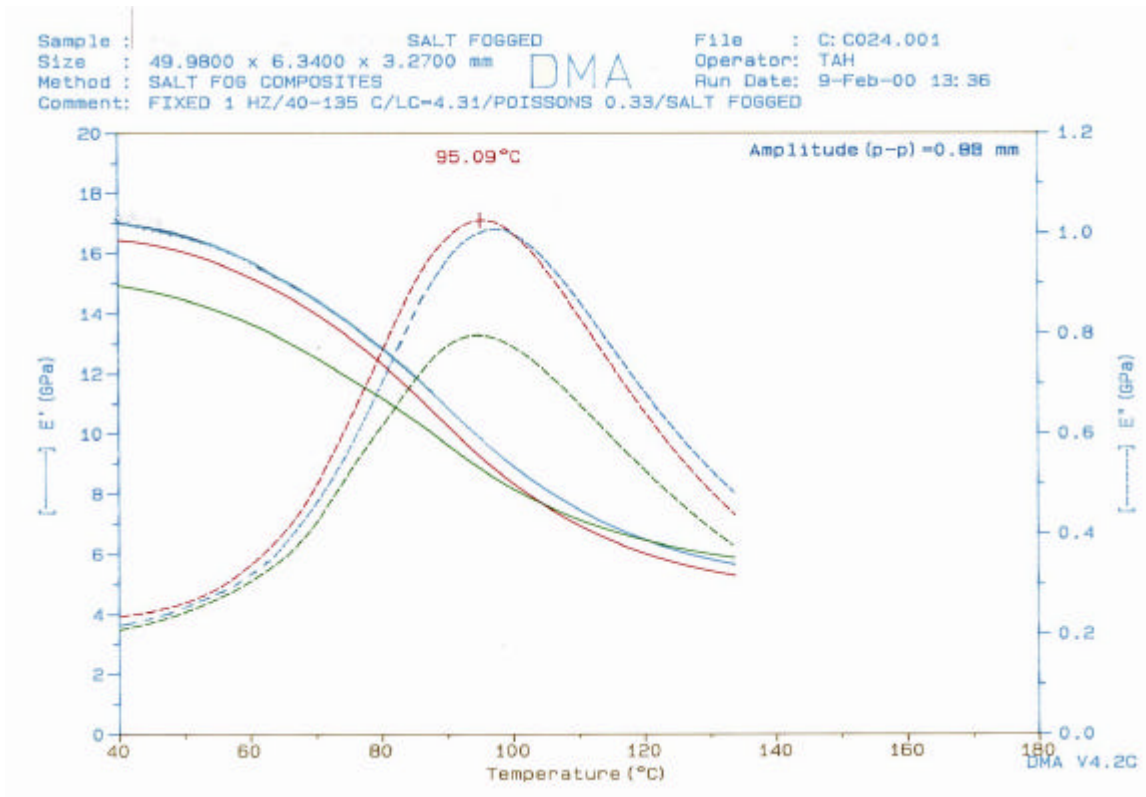
FIGURE D-11. DMA SALT FOG RESULTS FOR POLYESTER I.
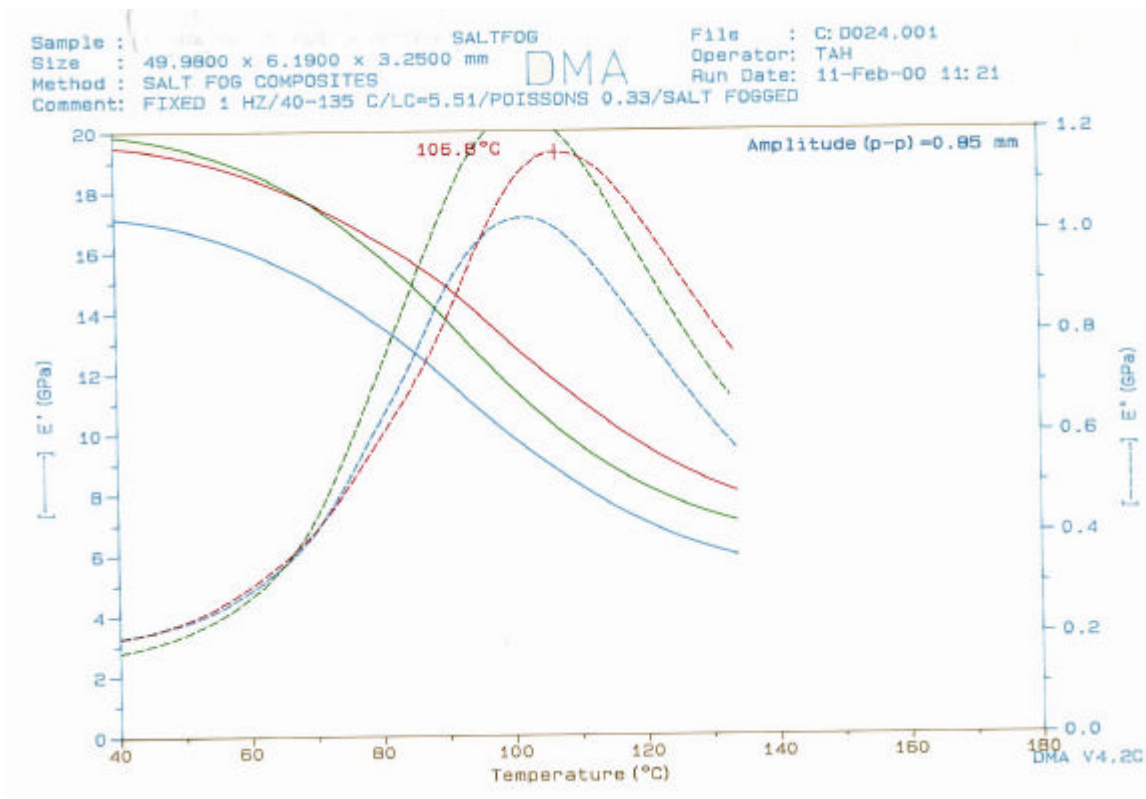
FIGURE D-12. DMA SALT FOG RESULTS FOR POLYESTER II.
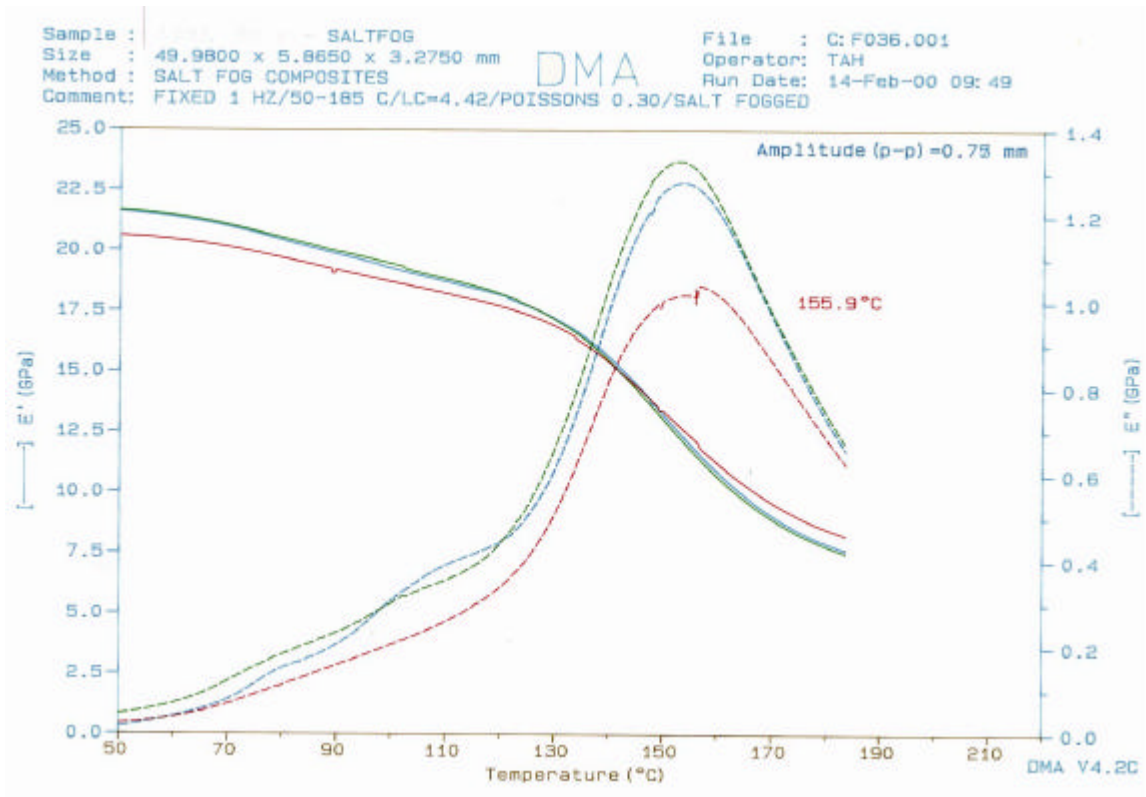
FIGURE D-13. DMA SALT FOG RESULTS FOR EPOXY.
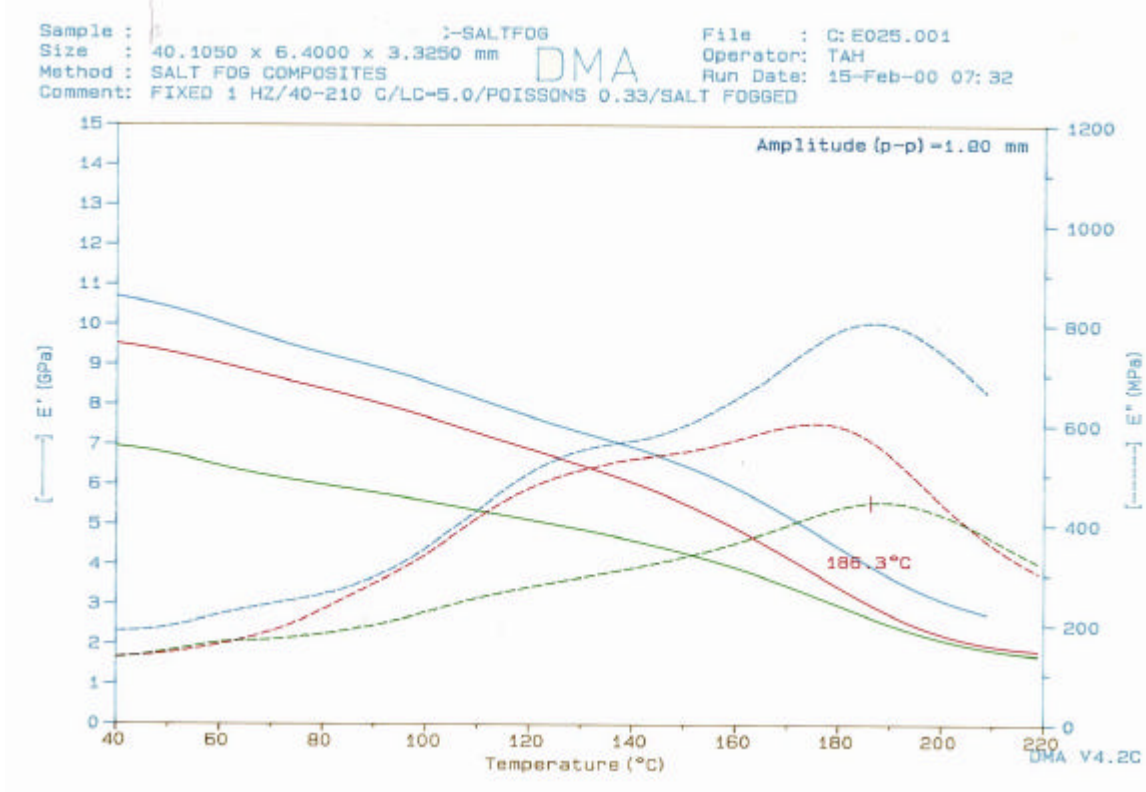
FIGURE D-14. DMA SALT FOG RESULTS FOR PHENOLIC II.
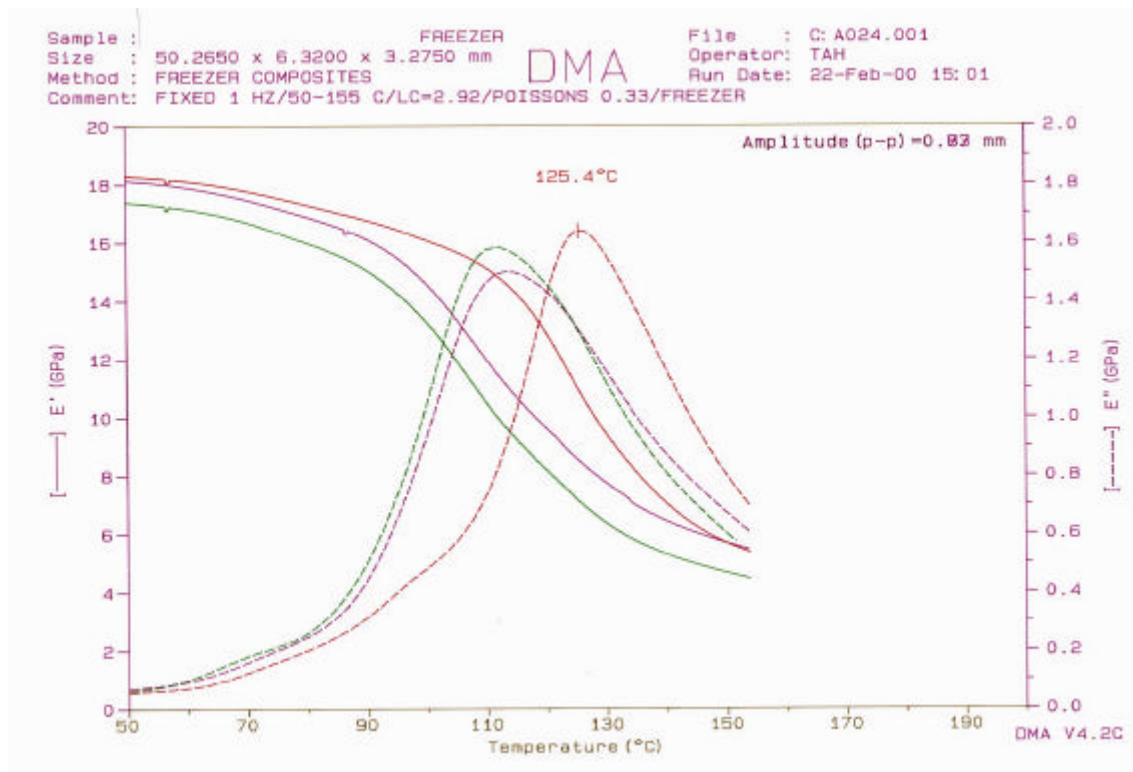
FIGURE D-15. DMA FREEZER RESULTS FOR VINYLESTER I.
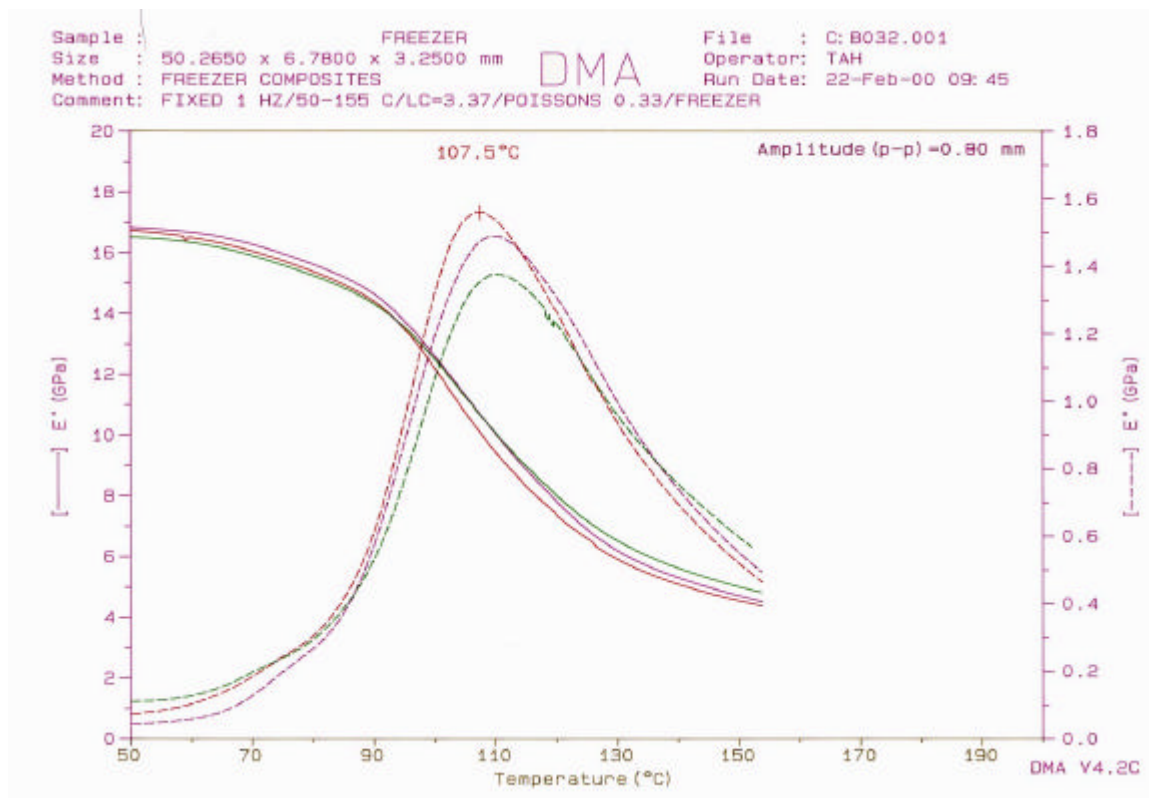
FIGURE D-16. DMA FREEZER RESULTS FOR VINYLESTER II.

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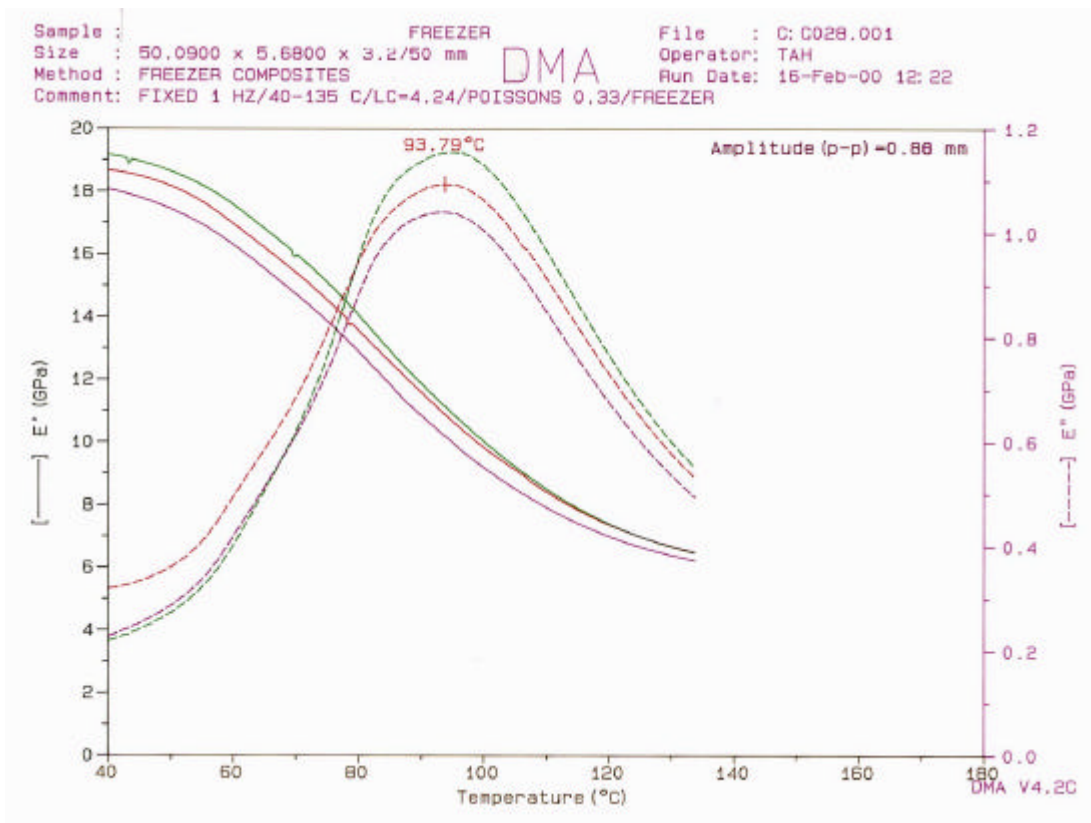
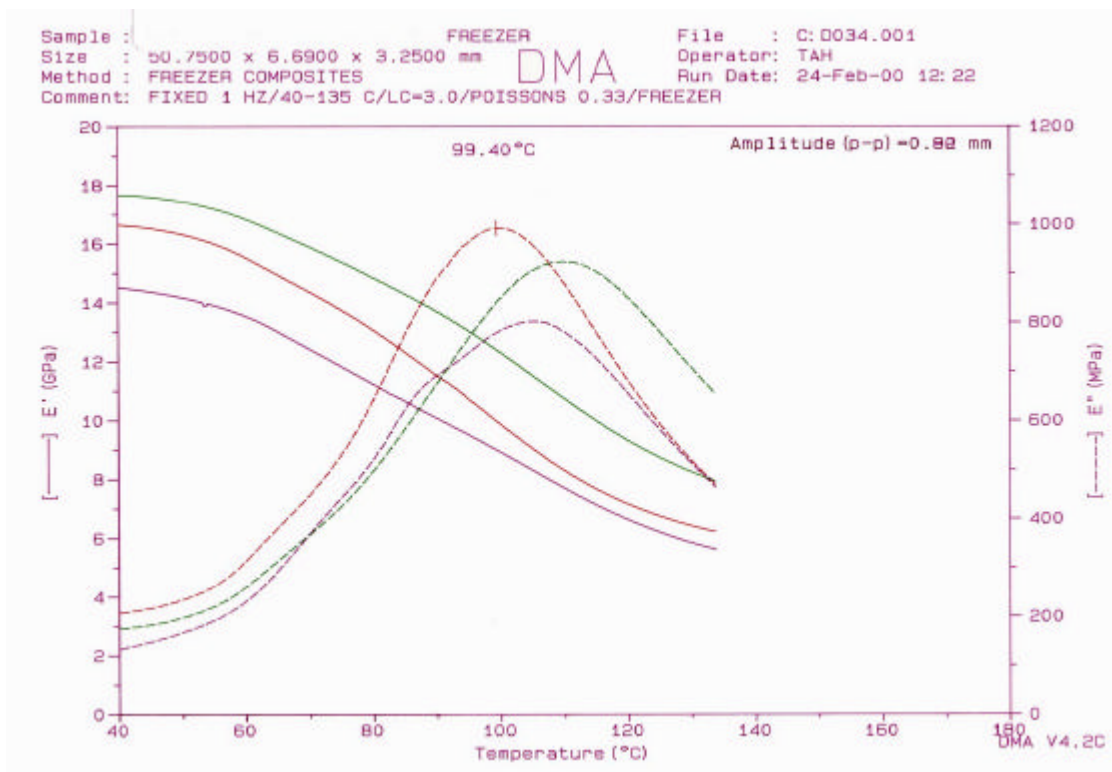FIGURE D-17. DMA FREEZER RESULTS FOR POLYESTER I.

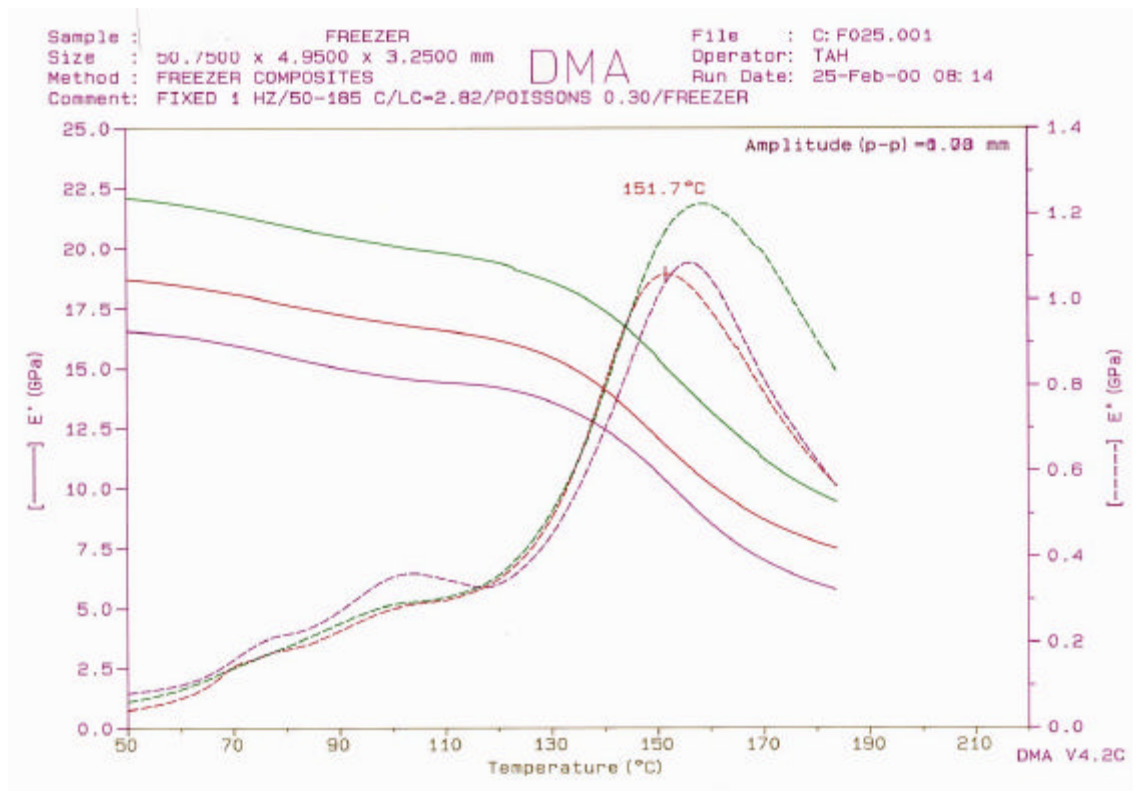FIGURE D-18. DMA FREEZER RESULTS FOR POLYESTER II.
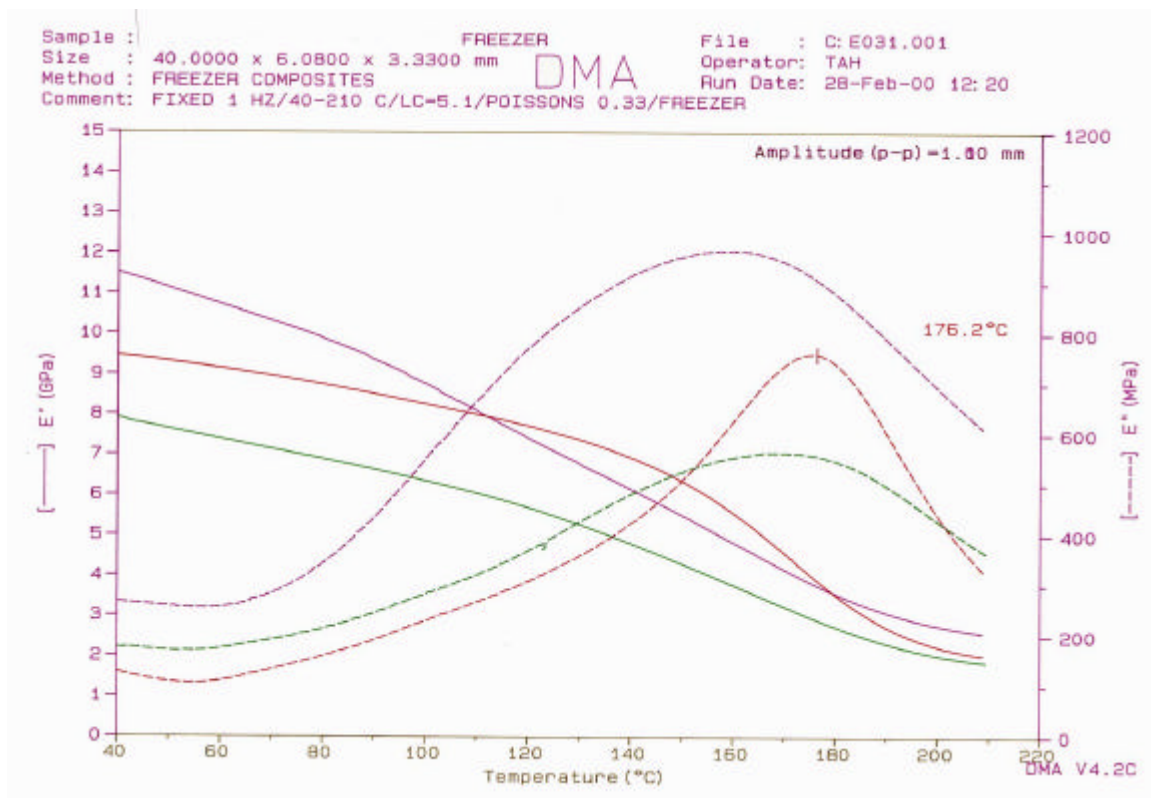
FIGURE D-19. DMA FREEZER RESULTS FOR EPOXY.

FIGURE D-20. DMA FREEZER RESULTS FOR PHENOLIC II.